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Synthesis of gold ferrocenyl substituted ylides and methanides: crystal structure of $[FcCH(AuPPh_3)PPh_3]ClO_4$ $[Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]$

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Abstract

The treatment of $[FcCH_2NMe_3]I$ with tertiary or ditertiary phosphines gives the phosphonium salts $[FcCH_2PR_3]I$ ($PR_3 = PPh_3$, PPh_2Me) or $[FcCH_2PPh_2CH_2PPh_2]I$. The reaction of $[FcCH_2PR_3]ClO_4$ with $[Au(acac)(PPh_3)]$ gives the ylide complexes $[FcCH(AuPPh_3)PR_3]ClO_4$. The compound $[FcCH_2PPh_2CH_2PPh_2]OTf$ reacts with several gold(I) complexes to give $[FcCH_2PPh_2CH_2PPh_2(AuCl)]OTf$, $[FcCH_2PPh_2CH_2PPh_2(AuC_6F_5)]OTf$ or $[FcCH_2PPh_2CH_2PPh_2(AuPPh_3)](OTf)_2$. The reaction of $[FcCH_2PPh_2CH_2PPh_2]ClO_4$ with $[O(AuPPh_3)_3]ClO_4$ leads to the methanide type species $[FcCH_2PPh_2C(AuPPh_3)_2PPh_2(AuPPh_3)](ClO_4)_2$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Gold complexes; Ferrocenyl complexes; Methanide complexes; Ylide complexes

1. Introduction

Ferrocene derivatives containing phosphorus groups have been the object of great attention in recent years [1]. Amongst them, the chemistry of 1,1′-bis(diphenylphosphino)ferrocene and its metal complexes has been extensively developed [2]. However, other derivatives in which the phosphorus atom is not directly bonded to the cyclopentadienyl ring are far less studied. The synthesis of the phosphonium salts $[FcCH_2PR_3]I$ [3] or the mixed phosphonium–phosphine salt $[FcCH_2PPh_2CH_2PPh_2]I$ [4] was reported some years ago. However, the coordination chemistry of these compounds has not been studied and only some sodium or potassium methanide complexes have been described.

Here we report on the reactivity of these phosphonium salts with several gold complexes. Thus, some ylide or methanide derivatives are synthesised and the crystal structure of the compound $[FcCH(AuPPh_3)PPh_3]ClO_4$ is described. Ylide [5] and methanide [6] complexes of gold have been previously reported and reviewed but no examples with ferrocene moieties have been described.

2. Experimental

2.1. General procedure

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 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 spectrometry (LSIMS) technique, using nitrobenzyl alcohol as the matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H, external) and 85% H_3PO_4 (^{31}P, external).

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2.2. Preparation of the compounds

The compounds [$FcCH_2PR_3$]I ($PR_3 = PPh_3$, PPh_2Me) [3], [$FcCH_2PPh_2CH_2PPh_2$]I [4], [Au(acac)(PPh_3)] [7], [O($AuPPh_3$)$_3$]ClO_4 [8], [AuCl(tht)] [9] and [Au(C_6F_5)(tht)] [10] were prepared by published procedures. [Au(OTf)(PR_3)] was obtained by reaction of equimolar amounts of [AuCl(PPh_3)] [11] and Ag(OTf).

2.2.1. [$FcCH_2PR_3$]ClO_4 ($PR_3 = PPh_3$ (**1**), PPh_2Me (**2**))

To a dichloromethane solution (30 ml) of [$FcCH_2PPh_3$]I (0.353 g, 0.6 mmol) or [$FcCH_2PPh_2Me$]I (0.315 g, 0.6 mmol) was added Ag(ClO_4) (0.124 g, 0.6 mmol). The mixture was stirred for 2 h and then the solid AgI formed was filtered. The solution was concentrated to ca. 5 ml and diethyl ether (20 ml) was added to yield yellow solids of **1** or **2**. Compound **1**, yield 86%. *Anal.* Calc. for $C_{29}H_{26}ClFeO_4P$: C, 62.11; H, 4.67. Found: C, 61.87; H, 4.37%. Λ_M 130 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR, δ: 3.90 (m, 2H, C_5H_4), 4.06 (m, 2H, C_5H_4), 4.30 (s, 5H, C_5H_5), 4.61 [d, 2H, CH_2, J(PH) 12.3 Hz], 7.2–7.6 (m, br, 15H, Ph). ^{31}P{^{1}H} NMR, δ: 19.8 (s) ppm. Compound **2**, yield 87%. *Anal.* Calc. for $C_{24}H_{24}ClFeO_4P$: C, 57.80; H, 4.85. Found: C, 57.34; H, 4.68%. Λ_M 135.5 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR, δ: 2.37 (m, br, 3H, PMe), 4.07–4.24 (m, br, 11H, $FcCH_2$), 7.64–7.74 (m, 10H, Ph). ^{31}P{^{1}H} NMR, δ: 19.6 (s) ppm.

2.2.2. [$FcCH_2PPh_2CH_2PPh_2$]X (X = ClO_4 (**3a**), OTf (**3b**))

To a solution of [$FcCH_2PR_2CH_2PPh_2$]I (0.710 g, 1 mmol) in dichloromethane (30 ml) was added Ag(ClO_4) (0.207 g, 1 mmol) or Ag(OTf) (0.026 g, 0.1 mmol) and the mixture was stirred for 2 h. Then the solid AgI was filtered and the solution concentrated to ca. 5 ml. Addition of diethyl ether (20 ml) gave a yellow solid of **3a** or **3b**. Compound **3a**: yield 95%. *Anal.* Calc. for $C_{36}H_{33}ClFeO_4P_2$: C, 63.32; H, 4.87. Found: C, 62.98; H, 4.55%. Λ_M 140 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR, δ: 3.66 [d, 2H, CH_2, J(PH) 13.91 Hz], 3.85 (m, 2H, C_5H_4), 3.96 (m, 2H, C_5H_4), 4.23 (s, 5H, C_5H_5), 4.41 [d, 2H, CH_2, J(PH) 11.53 Hz], 7.2–7.6 (m, br, 20H, Ph). ^{31}P{^{1}H} NMR, δ: 21.6 [d, 1P, C–P–C, J(PP) 50 Hz], −27.3 (d, 1P, C–P). Compound **3b**: yield 78%. *Anal.* Calc. for $C_{37}H_{33}F_3FeO_3P_2S$: C, 60.67; H, 4.54; S, 4.38. Found: C, 60.36; H, 4.55; S, 4.39%. Λ_M 120 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR, δ: 3.84 [d, 2H, CH_2, J(PH) 14.4 Hz], 4.0 (m, 2H, C_5H_4), 4.05 (m, 2H, C_5H_4), 4.19 (s, 5H, C_5H_5), 4.49 [d, 2H, CH_2, J(PH) 12.1 Hz], 7.2–7.6 (m, br, 20H, Ph). ^{31}P{^{1}H} NMR, δ: 23.3 [d, 1P, C–P–C, J(PP) 62.9 Hz], −28.2 (d, 1P, C–P).

2.2.3. [FcCH($AuPPh_3$)PR_3]ClO_4 ($PR_3 = PPh_3$ (**4**), PPh_2Me (**5**))

To a solution of [$FcCH_2PPh_3$]ClO_4 (0.056 g, 0.1 mmol) or [$FcCH_2PPh_2Me$]ClO_4 (0.050 g, 0.1 mmol) in dichloromethane (20 ml) was added [Au(acac)(PPh_3)] (0.059 g, 0.1 mmol) and the solution was stirred for 2 h. Evaporation of the solvent to ca. 5 ml and addition of diethyl ether (20 ml) afforded yellow solids of **4** or **5**. Complex **4**, yield 66%. *Anal.* Calc. for $C_{47}H_{40}AuClFeO_4P_2$: C, 55.39; H, 3.95. Found: C, 54.89; H, 3.88%. Λ_M 119.6 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR, δ: 3.82 (m, 2H, C_5H_4), 4.0 (m, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 4.3 (m, 1H, CH), 7.2–7.6 (m, br, 30H, Ph). ^{31}P{^{1}H} NMR, δ: 23.8 (m, 1P, $CHPPh_3$), 39.9 (m, 1P, $AuPPh_3$) ppm. Complex **5**, yield 71%. *Anal.* Calc. for $C_{42}H_{38}AuClFeO_4P_2$: C, 52.71; H, 4.00. Found: C, 53.11; H, 4.39%. Λ_M 156 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR, δ: 2.27 [d, 3H, J(PH) 12.61 Hz, PMe], 4.04 (m, 2H, C_5H_4), 4.06 (m, 2H, C_5H_4), 4.07 (s, 5H, C_5H_5), 4.18 [d, 1H, CH, J(PH) 12.0 Hz], 7.2–7.8 (m, br, 25H, Ph). ^{31}P{^{1}H} NMR, δ: 21.6 [d, 1P, J(PP) 9.2 Hz, $CHPPh_2Me$), 40.7 (d, 1P, $AuPPh_3$) ppm.

2.2.4. [$FcCH_2PPh_2CH_2PPh_2$(AuX)]OTf (X = Cl (**6**), C_6F_5 (**7**))

To a solution of [$FcCH_2PPh_2CH_2PPh_2$]OTf (0.073 g, 0.1 mmol) in dichloromethane (20 ml) was added [AuCl(tht)] (0.032 g, 0.1 mmol) or [Au(C_6F_5)(tht)] (0.045 g, 0.1 mmol) and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 ml and addition of diethyl ether (15 ml) gave complexes **6** or **7** as yellow solids. Complex **6**, yield 72%. *Anal.* Calc. for $C_{37}H_{33}AuClF_3FeO_3P_2S$: C, 46.05; H, 3.44; S, 3.32. Found: C, 45.89; H, 3.23; S, 3.56%. Λ_M 95.8 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR, δ: 3.92 (m, br, 2H, CH_2), 4.08 (m, br, 2H, CH_2), 4.26 (m, br, 9H, Fc), 7.3–7.9 (m, br, 20H, Ph). ^{31}P{^{1}H} NMR, δ: 17.7 (m, br, 1P), 19.0 (m, br, 1P) ppm. Complex **7**, yield 86%. *Anal.* Calc. for $C_{43}H_{33}AuF_8FeO_3P_2S$: C, 47.10; H, 3.03; S, 2.92. Found: C, 47.43; H, 3.21; S, 3.26%. Λ_M 114 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR, δ: 3.89 (m, 2H, C_5H_4), 4.06 (m, 2H, C_5H_4), 4.22 (s, 5H, C_5H_5), 4.36 [d, 2H, CH_2, J(PH) 13.2 Hz], 4.41 [d, 2H, CH_2, J(PH) 12.3 Hz], 7.2–7.8 (m, br, 20H, Ph). ^{31}P{^{1}H} NMR, δ: 19.6 (m, 1P, C–P–C), 25.5 [d, 1P, P–Au, J(PP) 9 Hz] ppm. ^{19}F NMR, δ: −116.7 (m, 2F, *o*-F), −157.4 [t, 1F, *p*-F, J(FF) 19.9 Hz], −162.1 (m, 2F, *m*-F).

2.2.5. [$FcCH_2PPh_2CH_2PPh_2Au(PPh_3)$](OTf)$_2$ (**8**)

To a solution of [$FcCH_2PR_2CH_2PPh_2$]OTf (0.073 g, 0.1 mmol) in dichloromethane (20 ml) was added [Au(OTf)(PPh_3)] (0.061 g, 0.1 mmol) and the mixture was stirred for 1 h. Concentration of the solution to ca. 5 ml and addition of diethyl ether afforded a yellow solid of **8**. Yield 95%. *Anal.* Calc. for $C_{56}H_{48}AuF_6FeO_6P_3S_2$: C, 50.16; H, 3.60; S, 4.78. Found: C, 49.62; H, 3.31; S, 4.87%. Λ_M 150 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR, δ: 4–5 ppm (br, overlapped, 9H, Fc + CH_2), 7–8 (m, br, 35H, Ph). ^{31}P{^{1}H} NMR, ABX system, δ_X 20.0 (m, 1P, C–P–C), δ_A 31.0, δ_B 44.2 ppm (P–Au–P), J(AB) 326 Hz.

2.2.6. $[FcCH_2PPh_2C(AuPPh_3)_2PPh_2Au(PPh_3)](ClO_4)_2$ (9)

To a solution of $[FcCH_2PPh_2CH_2PPh_2]ClO_4$ (0.068 g, 0.1 mmol) in dichloromethane (20 ml) was added $[O(AuPPh_3)_3]ClO_4$ (0.149 g, 0.1 mmol) and the mixture was stirred for 2 h. Concentration of the solution to ca. 5 ml and addition of diethyl ether (10 ml) led to a yellow solid of **9**. Yield 86%. *Anal.* Calc. for $C_{90}H_{76}Au_3Cl_2FeO_8P_5$: C, 50.09; H, 3.55. Found: C, 49.87; H, 3.54%. Λ_M 199 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR, δ: 3.41 [d, 2H, CH_2, J(PH) 12.1 Hz, CH_2–P], 3.88 (s, 5H, C_5H_5), 3.98 (m, 2H, C_5H_4), 4.24 (m, 2H, C_5H_4), 7–8 (m, br, 65H, Ph). ^{31}P{^{1}H} NMR, ABM_2X system, δ_A 45.6, δ_B 53.3 (P–Au–P), J(AB) 317 Hz, δ_M 36.2 (m, 2P, PPh_3), δ_X 28.3 (m, 1P, C–P–C) ppm.

2.3. X-ray structure determination of complex 4

Crystals of **4** were grown from dichloromethane/hexane. A yellow prism of 0.55 × 0.25 × 0.20 mm was mounted in inert oil on a glass fibre. A total of 9910 intensities were registered using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å, $2\theta_{max} = 50°$) on a Siemens P4 four circle diffractometer; 7033 unique reflections ($R_{int} = 0.0848$) and 6983 were used for all calculations. Cell constants were refined from setting angles of 60 reflections in the range $2\theta = 10–25°$. An absorption correction based on Ψ-scans was applied, with transmission factors 0.760–0.941. The structure was solved by direct methods and all the atoms were refined anisotropically on F^2 using the program SHELXL-93 [12]. H atoms were included using a riding model. The final $wR(F^2)$ was 0.159 for all reflections, with a conventional $R(F)$ of 0.0526, for 505 parameters. $S = 1.035$; max. $\Delta\rho = 1.674$ e Å^{-3}. Further details are shown in Table 1.

Table 1
Details of data collection and structure refinement for complex **4**

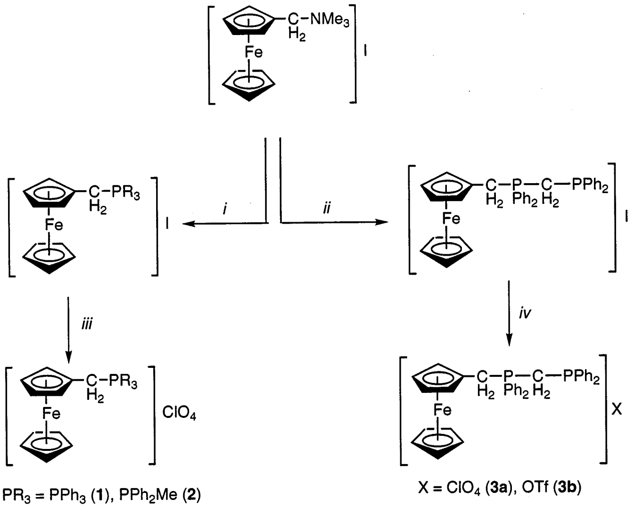
Empirical formula	$C_{47}H_{40}AuClFeO_4P_2$
Formula weight	1019
Space group	$P2_1/c$
V(Å^3)	4124.6(7)
Z	4
D_{calc} (g cm^{-3})	1.641
a (Å)	10.9310(10)
b (Å)	32.850(4)
c (Å)	11.8070(10)
β (°)	103.381(7)
T (K)	173
μ(Mo Kα) (mm^{-1})	4.091
R^a (F, $F>4\sigma(F)$)	0.0526
wR^b(F^2, all reflections)	0.159

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$.

3. Results and discussion

The reaction of $[FcCH_2NMe_3]I$ with tertiary phosphines affords the previously synthesised phosphonium salts $[FcCH_2PR_3]I$ ($PR_3 = PPh_3$, PPh_2Me). In order to react them with gold complexes we have changed the anion iodide to perchlorate by reacting $[FcCH_2PR_3]I$ with $AgClO_4$ (Scheme 1). The new compounds $[FcCH_2PR_3]ClO_4$ ($PR_3 = PPh_3$ (**1**), PPh_2Me (**2**)) are air and moisture stable yellow solids that behave as 1:1 electrolytes in acetone solutions. Their IR spectra show the bands arising from the phosphine and ferrocenyl groups and those of the perchlorate anion around 1100 (vs, br) and 620 (m) cm^{-1}. In their ^{1}H NMR spectra appear two multiplets for the α and β protons of the substituted cyclopentadienyl group, a singlet for the protons of the unsubstituted Cp ring and a doublet for the methylene protons. Compound **2** also shows a doublet for the phosphine methyl protons. The ^{31}P{^{1}H} NMR spectra present one singlet for the phosphorus atom.

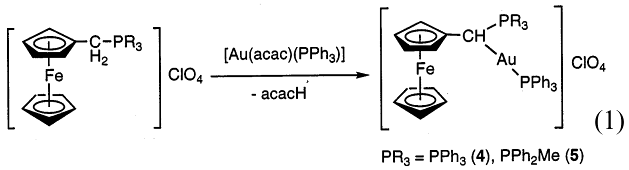
We have also prepared the compound $[FcCH_2PPh_2CH_2PPh_2]X$ ($X = ClO_4$ (**3a**), OTf (**3b**)) by reaction of the previously known $[FcCH_2PPh_2CH_2PPh_2]I$ with $Ag(ClO_4)$ or Ag(OTf) (Scheme 1). Compound **3a** also shows in its IR spectrum the absorptions of the perchlorate anion at 1095 (vs, br) and 623 (m) cm^{-1}, whereas **3b** shows the absorptions of the triflate anion at 1265(vs, br) [$\nu_{as}(SO_3)$], 1223(s) [$\nu_s(CF_3)$], 1150(s) [$\nu_{as}(CF_3)$] and 1023(s) [$\nu_s(SO_3)$] cm^{-1}. The ^{1}H NMR spectrum presents two multiplets for the α and β protons of thesubstituted Cp and a singlet for the protons of the unsubstituted Cp ring and a doublet for each methylene group. Surprisingly, no coupling with



Scheme 1. (i) PR_3, (ii) $PPh_2CH_2PPh_2$, (iii) $Ag(ClO_4)$, (iv) $Ag(ClO_4)$ or Ag(OTf).

one of the phosphorus atoms is observed for the P–*CH*$_2$–P group, but a doublet was also observed in the starting material [FcCH$_2$PPh$_2$CH$_2$PPh$_2$]I [4]. In the ^{31}P{^{1}H} NMR spectrum two doublets for the two phosphorus atoms with coupling between them appear. The chemical shift is characteristic of a phosphonium phosphorus, ≈ 21 ppm, and uncoordinated phosphine ligand, ≈ -27 ppm.

The treatment of the phosphonium salts **1** or **2** with [Au(acac)(PPh$_3$)] leads to complexes [FcCH(AuPPh$_3$)-PR$_3$]ClO$_4$ (PR$_3$ = PPh$_3$ (**4**), PPh$_2$Me (**5**)) originated by substitution of one proton of the methylene group by the isolobal fragment AuPPh$_3^+$; acetylacetone is formed in the reaction (Eq. 1).



(1)

The use of acetylacetonato (acac) complexes has been previously reported in the synthesis of ylide and methanide gold derivatives [13–15]. Complexes **4** and **5** are air and moisture stable yellow solids that behave as 1:1 electrolytes in acetone solutions.

In the ^{1}H NMR spectrum of **4** and **5** the protons of the substituted cyclopentadienyl ring appear as two multiplets, the protons of the unsubstituted Cp ring appear as a singlet, whereas the CH proton appears as a doublet of doublets in complex **4** as a consequence of the coupling with both phosphorus atoms and as a doublet for complex **5**. The methyl protons in **5** appear also as a doublet. The ^{31}P{^{1}H} NMR spectra show two doublets for the two different phosphorus environments with coupling between them.

In the liquid secondary positive-ion mass spectra the cationic molecular peaks appear at $m/z = 919$ (**4**, 15%) and 857 (**5**, 71%); the fragments arising from the loss of PPh$_3$ are also present at 657 (**4**, 90%) and 594 (**5**, 6%).

The molecular structure of complex **4** has been confirmed by an X-ray diffraction study and the cation is shown in Fig. 1. A selection of bond lengths and angles are collected in Table 2. The gold atom has a linear geometry with an almost ideal angle of 178.2(3)°. The Au–C distance is 2.089(9) Å and is of the same order as those found in other ylide or methanide complexes such as [Au(C$_6$F$_5$)$_2${μ-(PPh$_2$)$_2$CH(AuC$_6$F$_5$)}] (2.094(7) Å) [16]. The Au–P bond distance of 2.274(3) Å is similar to complexes which have a carbon ligand *trans* to the phosphorus.

The cyclopentadienyl rings are staggered by 10° around the Cp···Cp axis defined by the torsion angle C(1)–centre–centre–C(8). The distances of the Fe atom to the centres of the rings are 1.651 and 1.659 Å which compare well with the values reported for other ferrocene moieties, as do the Fe–C distances. In some gold or silver complexes with ferrocene derivatives as ligands, we have observed the presence of weak η^2 interactions between the metal centres and two of the carbons of the cyclopentadienyl ring [17,18]. In this complex, the Au···C(1) and Au···C(5) distances are around 3.5 Å and, thus, although very weak, point out the existence of possible bonding interaction.

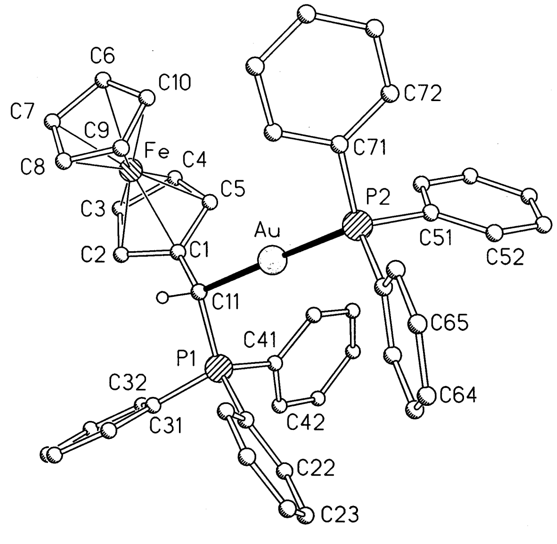
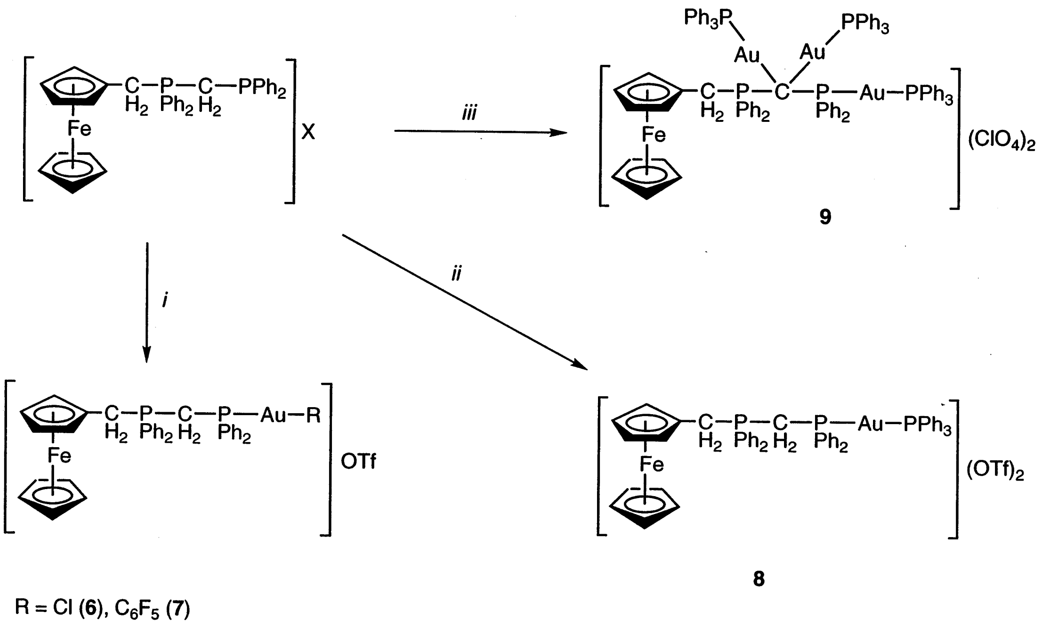


Fig. 1. Structure of the cation of complex **4** in the crystal showing the atom-numbering scheme. Radii are arbitrary. The Cp and Ph hydrogen atoms are omitted for clarity.

We have also studied the reaction of compound **3b** with several gold complexes. First, the treatment of **3b** with [AuR(tht)] (tht = tetrahydrothiophene), which possesses the labile ligand tht, leads to the gold complexes [FcCH$_2$PPh$_2$CH$_2$PPh$_2$(AuR)]OTf (R = Cl (**6**), C$_6$F$_5$ (**7**)) by coordination of the gold centre to the phosphine phosphorus atom. Complexes **6** and **7** are yellow solids,

Table 2
Selected bond lengths (Å) and angles (°) for **4**

Au–C(11)	2.089(9)	Au–P(2)	2.274(3)
P(1)–C(41)	1.802(9)	P(1)–C(31)	1.807(9)
P(1)–C(21)	1.810(10)	P(1)–C(11)	1.811(8)
P(2)–C(71)	1.818(10)	P(2)–C(61)	1.821(11)
P(2)–C(51)	1.824(11)	C(1)–C(11)	1.503(13)
C(11)–Au–P(2)	178.2(3)	C(41)–P(1)–C(31)	108.7(4)
C(41)–P(1)–C(21)	110.6(4)	C(31)–P(1)–C(21)	105.4(4)
C(41)–P(1)–C(11)	111.7(4)	C(31)–P(1)–C(11)	111.0(4)
C(21)–P(1)–C(11)	109.4(5)	C(71)–P(2)–C(61)	106.0(5)
C(71)–P(2)–C(51)	107.2(5)	C(61)–P(2)–C(51)	105.4(5)
C(71)–P(2)–Au	112.5(4)	C(61)–P(2)–Au	113.4(3)
C(51)–P(2)–Au	111.9(4)	C(1)–C(11)–P(1)	110.9(6)
C(1)–C(11)–Au	119.9(6)	P(1)–C(11)–Au	108.3(4)
C(26)–C(21)–P(1)	120.9(8)	C(22)–C(21)–P(1)	118.4(9)
C(32)–C(31)–P(1)	124.0(8)	C(36)–C(31)–P(1)	116.3(7)
C(42)–C(41)–P(1)	121.8(7)	C(46)–C(41)–P(1)	119.2(7)
C(56)–C(51)–P(2)	118.4(9)	C(52)–C(51)–P(2)	122.9(8)
C(66)–C(61)–P(2)	123.4(9)	C(62)–C(61)–P(2)	118.5(8)
C(76)–C(71)–P(2)	118.7(8)	C(72)–C(71)–P(2)	122.8(8)



Scheme 2. (i) X = OTf, [AuCl(tht)] or [Au(C_6F_5)(tht)], (ii) X = OTf, [Au(OTf)(PPh_3)], (iii) X = ClO_4, [O($AuPPh_3$)$_3$]ClO_4.

air and moisture stable that behave as 1:1 electrolytes in acetone solutions. Their IR spectra show the presence of the ν(Au–Cl) band at 335 (m) cm^{-1} and the bands assigned to a pentafluorophenyl group bonded to Au(I) at 1504 (s), 955 (s) and 793 (m) cm^{-1}. In the ^1H NMR spectra, the resonances of the methylene groups appear as doublets for complex **7**, whereas in **6** there are broad singlets. The resonances of the ferrocene moiety appear as two multiplets and a singlet in the appropriate 2:2:5 ratio. The $^{31}P\{^1H\}$ NMR spectra show two signals corresponding to two different phosphorus environments; for complex **7** the signals are better resolved and appear as doublets. The ^{19}F spectrum of **7** presents three resonances for the *ortho*, *meta* and *para* fluorines of the pentafluorophenyl group.

In the positive liquid secondary ion mass spectra (LSIMS +) of complexes **6** and **7** the molecular peaks appear at $m/z = 815$ (**6**, 68%) and 947 (**7**, 100%).

The reaction of **3b** with [Au(OTf)(PPh_3)] leads to the dicationic complex [$FcCH_2PPh_2CH_2PPh_2$($AuPPh_3$)]$(OTf)_2$ (**8**) in high yield. Complex **8** is an air and moisture stable yellow solid that behaves as a 1:2 electrolyte in acetone solutions. Its ^1H NMR spectrum shows broad resonances (even when the experiment is carried out at low temperature) between 4 and 5 ppm which correspond to the methylene and ferrocenyl protons. The $^{31}P\{^1H\}$ NMR spectrum presents an ABX system. The AB part corresponds to the PPh_2–Au–PPh_3 unit, with a large coupling constant of 326 Hz.

In the LSIMS + mass spectrum, the molecular peak appears at $m/z = 1340$ (7%), although with low intensity. However, the fragments at $m/z = 1191$ (12%) and 1041 (100%) due to the loss of one or two triflate anions are more intense.

Finally, we have synthesised a methanide gold derivative, [$FcCH_2PPh_2C(AuPPh_3)_2PPh_2(AuPPh_3)$]$(ClO_4)_2$ (**9**), by reacting [$FcCH_2PPh_2CH_2PPh_2$]ClO_4 with [O($AuPPh_3$)$_3$]ClO_4 (Scheme 2); the oxonium salt has already proved to be a good deprotonating agent in the synthesis of gold complexes. The most acidic methylene protons, which are those in between both phosphorus atoms, are removed and substituted by the isolobal fragment $AuPPh_3^+$. Complex **9**, with a different counterion, can also be obtained by treatment of **8** with two equivalents of [Au(acac)(PPh_3)]. Compound **9** is a pale-yellow air and moisture stable solid that behaves as electrolyte 1:2 in acetone solutions. Its IR spectrum shows, in addition to the bands arising at the ferrocene and phenyl groups, the ν(Au–C) vibration at 536 (w) cm^{-1}. In the ^1H NMR spectrum, the methylene protons appear as a doublet, the α and β protons of the C_5H_4 ring as multiplets and the C_5H_5 protons as a singlet. The $^{31}P\{^1H\}$ NMR spectrum presents an ABM_2X system. Again the AB part corresponds to the PPh_2–Au–PPh_3 unit. The signals of the B nuclei appear as multiplets because the coupling with M and/or X nuclei and the signals of M and X are multiplets. In the LSIMS + mass spectrum, the molecular peak does not appear but the fragment due to the loss of one ClO_4^- anion does at $m/z = 2057$ (12%) with coincident experimental and calculated isotopic distribution.

4. Supplementary material

Tables listing crystallographic data, positional and thermal parameters, and complete bond lengths and angles for complex **4** are available from the authors on request.

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References

[1] A. Togni, T. Hayashi (Eds.), Ferrocenes: Homogeneous Catalysis, Organic Synthesis and Materials Science, VCH, Weinheim, 1995.

[2] K.S. Gan, T.S.A. Hor, in: A. Togni, T. Hayashi (Eds.), Ferrocenes: Homogeneous Catalysis, Organic Synthesis and Materials Science, VCH, Weinheim, 1995, Ch. 1 and Refs. therein.

[3] P.L. Pauson, W.E. Watts. J. Chem. Soc. (1963) 2990.

[4] H. Schmidbaur, U. Deschler, D. Seyferth, Z. Naturforsch., Teil B 37 (1982) 950.

[5] A. Grohmann, H. Schmidbaur, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprenhensive Organometallic Chemistry II, vol. 3, Pergamon, Oxford, 1995, p. 1.

[6] A. Laguna, M. Laguna, J. Organomet. Chem. 394 (1990) 743.

[7] (a) D. Gibson, B.F.G. Johnson, J. Lewis, J. Chem. Soc., A (1970) 367. (b) J. Vicente, M.T. Chicote, Inorg. Synth. 32 (1998) 172.

[8] A.N. Nesmeyanov, E.G. Perevalova, Yu.T. Struchkov, M.Yu. Antipin, K.I. Grandberg, V.P. Dyadchenko, J. Organomet. Chem. 201 (1980) 343.

[9] R. Usón, A. Laguna, M. Laguna, Inorg. Synth. 26 (1989) 85.

[10] R. Usón, A. Laguna, J. Vicente, J. Chem. Soc., Chem. Commun. (1976) 353.

[11] R. Usón, A. Laguna, Inorg. Synth. 21 (1982) 71.

[12] G.M. Sheldrick, SHELXL-93: Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.

[13] J. Vicente, M.T. Chicote, M.C. Lagunas, Inorg. Chem. 32 (1993) 3748 and Refs. therein.

[14] M.C. Gimeno, A. Laguna, M. Laguna, F. Sanmartín, P.G. Jones, Organometallics 12 (1993) 3984.

[15] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, J.M. López de Luzuriaga, J. Chem. Soc., Dalton Trans. (1992) 3365.

[16] R. Usón, A. Laguna, M. Laguna, B. Manzano, P.G. Jones, G.M. Sheldrick, J. Chem. Soc., Dalton Trans. (1984) 839.

[17] O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, C. Sarroca, J. Chem. Soc., Chem. Commun. (1998) 1481.

[18] M.J. Calhorda, M.C. Gimeno, P.G. Jones, A. Laguna, C. Sarroca, L. Veiros, Chem. Eur. J. 4 (1988) 2308.