

Gold Chemistry with Ferrocene Derivatives as Ligands

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The synthesis and properties of gold complexes with 1,1'-bis(diphenylphosphino)ferrocene (dppf), its sulfide (dppfS₂) and disubstituted dithiocarbamate or thiolate ferrocene derivatives as ligands are reviewed. The ability of these metalloligands to modify their steric bite in order to adapt to different geometric requirements of the metal centres has allowed the synthesis of several gold complexes with unusual geometries and novel structures. The potential of the new compounds for a number of applications is considered.

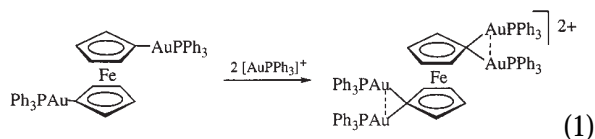
Organometallic ligands provide a convenient route to the synthesis of heterometallic complexes. Amongst these ligands ferrocene derivatives have been the most widely studied. Due to the high stability of ferrocenes and the well-established methods for their incorporation into more complex structures, they have become versatile building blocks for the synthesis of compounds with tailor-made properties (1-4). Ferrocene-containing complexes are currently receiving much attention associated with their widespread utility, *eg* in organic synthesis, production of fine chemicals, homogeneous catalysis, and materials chemistry.

Numerous derivatives have been reported in which the cyclopentadienyl rings of ferrocene carry organic groups with one or more donor atoms. An important feature of these potential ligands is their flexibility: the bidentate representatives can adapt as chelating groups to different geometric requirements of a given metal centre and act as bridging ligands. Some of the complexes obtained with these ligands have interesting redox properties and unusual structures (1-4). The coordination of ferrocene and of mono- or di- substituted diphenylphosphino, diphenylthiophosphoryl, dithiocarbamate and thiolate derivatives to gold(I) and gold(III) leads to interesting three- or four-coordinate mono- and polynuclear gold complexes.

FERROCENYL COMPLEXES

Ferrocenylgold compounds with the gold centre directly attached to the cyclopentadienyl rings were the

first derivatives of this type to be reported (5, 6). By reaction of the corresponding organolithium derivatives with [AuPPh₃]⁺ precursors the mono- and di-aurated complexes, [(C₅H₅)Fe(C₅H₄AuPPh₃)] and [Fe(C₅H₄AuPPh₃)₂], could be obtained (7). These complexes can incorporate additional [AuPPh₃]⁺ fragments, to give [(C₅H₅)Fe(C₅H₄)(AuPPh₃)₂]⁺ or [Fe{(C₅H₄)(AuPPh₃)₂}₂]²⁺ (6, 7) as is shown in Equation 1:

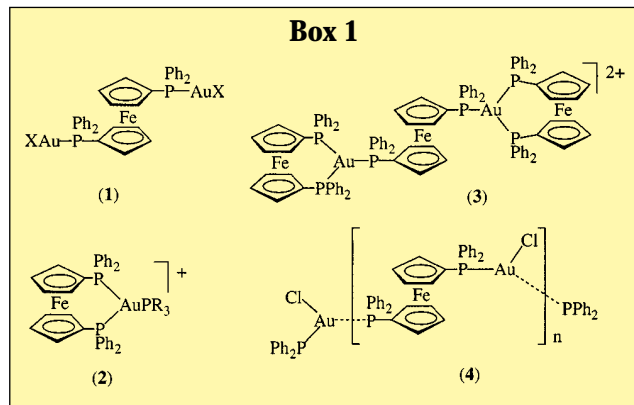


The bonding situation in the latter complexes has been described in terms of 3-centre-2-electron bonding, but resonance structures in which the aromaticity of the ring is lost and the positive charge delocalized over the ring are also acceptable. The short Au...Au distances (2.77 Å) and narrow Au-C-Au angles (78°) are indicative of a strong interaction between the gold centres.

COMPLEXES WITH P-SUBSTITUTED FERROCENE LIGANDS

The diphosphine 1,1'-bis(diphenylphosphino)ferrocene (dppf) has received a great deal of attention due to its chemical uniqueness and industrial importance (1). It

can act as a bridging or chelating ligand in two-, three-, and four-coordinated gold(I) and gold(III) compounds. Displacement of tetrahydrothiophene (tht) in gold(I) complexes such as $[\text{AuX}(\text{tht})]$ ($\text{X}=\text{Cl}$, C_6F_5), $[\text{Au}(\text{tht})\text{L}]\text{ClO}_4$ ($\text{L}=\text{phosphine}$, ylide) or $[\text{Au}(\text{tht})_2]\text{ClO}_4$ by the diphosphine leads to neutral representatives $[(\text{dppf})(\text{AuX})_2]$ (**1**) (Box 1), to cationic dinuclear complexes $[(\text{dppf})(\text{AuL})_2](\text{ClO}_4)_2$ and to three- and four-coordinate mononuclear derivatives $[(\text{dppf})\text{AuPR}_3]\text{ClO}_4$ (**2**) and $[\text{Au}(\text{dppf})_2]\text{ClO}_4$ (**8a**) respectively. The crystal structure of $[(\text{dppf})\text{AuPPh}_3]\text{ClO}_4$ indicates a trigonal-planar Au coordination. The Au-P distances (2.343 - 2.409 Å) are shorter than the Ag-P ones (2.424 - 2.480 Å) in the analogous $[(\text{dppf})\text{AgPPh}_3]\text{ClO}_4$ (**8b**), in agreement with theoretical predictions (**8c**). $[\text{Au}(\text{dppf})_2]\text{ClO}_4$ undergoes a dimerization process with liberation of one dppf and formation of $[(\text{dppf})\text{Au}(\mu\text{-dppf})\text{Au}(\text{dppf})](\text{ClO}_4)_2$ (**3**) which contains bridging and chelating diphosphines (**8b**). The same dication is present in $[(\text{dppf})\text{Au}(\mu\text{-dppf})\text{Au}(\text{dppf})](\text{NO}_3)_2$, obtained by the reaction of dinuclear $[(\text{dppf})(\text{AuCl})_2]$ with AgNO_3 and NaHCO_3 (**9**). Cyclic voltammetry of some of these compounds reveals one chemically reversible phosphinoferrocene-based oxidation (**9**).



Similar complexes, such as the dinuclear $[(\text{dppomf})(\text{AuX})_2]$ ($\text{X}=\text{Cl}$, C_6F_5) or the mononuclear three-coordinate compounds $[(\text{dppomf})\text{AuX}]$ can be obtained using the related diphosphine 1,1'-bis(diphenylphosphino)octamethylferrocene (dppomf) (**10**). The gold atom is trigonal planar in $[(\text{dppomf})\text{AuCl}]$. Electrochemical studies (**10**) show 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 $[\text{FeCp}_2]^+$. The cytotoxic properties of these complexes have been studied, but

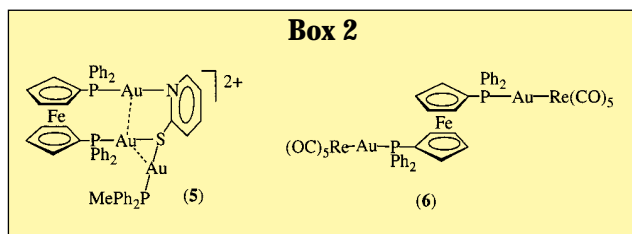
they show no superior properties to those for compounds evaluated previously (**10**).

The reaction of dppf with $[\text{AuCl}(\text{SR}_2)]$ leads to the formation of the chloro complexes $[(\text{dppf})(\text{AuCl})_2]$ (**1**, $\text{X}=\text{Cl}$), $[\text{AuCl}(\text{dppf})]$ and $[\text{AuCl}(\text{dppf})_2]$, depending on the molar ratio used (**8**, **9**, **12**, **13**). The ^{197}Au and ^{57}Fe Mössbauer and ^{31}P NMR spectroscopic data of the products indicate the existence of two different gold(I) coordination geometries in the solid state: linear and trigonal (**11**). The dinuclear $[(\text{dppf})(\text{AuCl})_2]$ has only marginal activity against the P388 leukaemia mouse model (**12**). The crystal structure of one of its known modifications shows a nearly linear P-Au-Cl unit and intermolecular gold-gold contacts of 3.083(1) Å (**12**), whereas no $\text{Au}\cdots\text{Au}$ interactions have been found in other modifications of the same compound (**14**). The reaction of $[(\text{dppf})(\text{AuCl})_2]$ with dppf (1:1 molar ratio) gives $[\text{AuCl}(\text{dppf})]$ as an intermediate, which readily polymerizes to give a chain polymer based on trigonal ClAuP_2 units (**4**) (**9**, **13**).

From $[(\text{dppf})(\text{AuCl})_2]$ other dinuclear complexes $[(\text{dppf})(\text{AuX})_2]$ ($\text{X}=\text{Br}$, I , 2-pyridinethiolate (Spy) or S_2CNR_2) can be obtained (**14**). The complex $[(\text{dppf})(\text{AuSpy})_2]$ with its nitrogen donor atom can coordinate to $[\text{AuPPh}_2\text{Me}]^+$ units to give the polynuclear compounds $[(\text{dppf})\{\text{AuSpy}(\text{AuPPh}_2\text{Me})\}_2](\text{OTf})_2$ ($\text{OTf}=\text{CF}_3\text{SO}_3$) and $[(\text{dppf})\{\text{AuSpy}(\text{AuPPh}_2\text{Me})_2\}_2](\text{OTf})_4$. The latter decomposes in solution and the trinuclear complex $[\text{Au}_3(\mu\text{-dppf})(\mu^3\text{-Spy})(\text{PPh}_2\text{Me})](\text{OTf})_2$ (**5**) (Box 2) is obtained, which represents the first example where a pyridinethiolate ligand bridges three gold centres. The gold atoms have geometries slightly distorted from linearity, probably due to the weak gold-gold interactions (3.0985(12) and 3.2105(13) Å) (**14**).

The reaction of $[(\text{dppf})(\text{AuCl})_2]$ with an excess of LiR in diethyl ether affords the organogold(I)-dppf complexes $[(\text{dppf})(\text{AuR})_2]$ [$\text{R}=\text{Me}$, Ph , 1-naphthyl, 9-anthryl, pyren-1-yl(C_{16}H_9), $\text{C}\equiv\text{CPh}$, $\text{C}\equiv\text{CBu}^t$]. Their photophysical and electrochemical properties have been studied (**15**). Excitation of these complexes at $\lambda > 330$ nm gives weak emissions in dichloromethane solutions. The electrochemical data show a quasi-reversible wave, due to the oxidation of the dppf, and an irreversible one assigned to $\text{Au}(\text{I}) \rightarrow \text{Au}(\text{II})$ oxidation. The structure of $[(\text{dppf})\{\text{Au}(\text{C}_{16}\text{H}_9)\}_2]$ is similar to that of the chloro derivative. The heterometallic complexes $[(\text{dppf})(\text{Au}\{\text{M}(\text{CO})_5\})_2]$ ($\text{M}=\text{Mn}$, Re) (**6**) are obtained by the reaction of $[(\text{dppf})(\text{AuCl})_2]$ with $\text{Na}[\text{M}(\text{CO})_5]$ (**16**). However, reaction with $\text{K}_2[\text{Pd}(\text{CN})_4]$ results in ligand

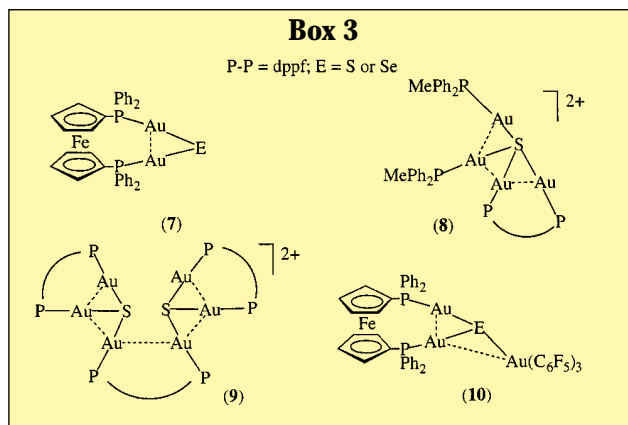
displacement with formation of [(dppf){Au(CN)}₂] instead of metal-metal bond formation. The X-ray photoelectron spectroscopic data for complex **6** suggest a polarization of the Au^{δ+}-Re^{δ-} bonds (16). The complexes [M(CO)₅(dppf)] (M = Cr, Mo, W) behave like a monodentate phosphine ligand and react with [AuCl(SMe₂)] to yield the heterometallic complex [M(CO)₅(μ-dppf)AuCl] (17).



Treatment of [(dppf)(AuCl)₂] with Li₂S (molar ratio 1:1) gives [S(Au₂dppf)] (**7**) (Box 3), in which the sulfur atom can further coordinate neutral or cationic gold(I) fragments to give the trinuclear complexes [S{Au(C₆F₅)}(Au₂dppf)] and [S(AuL)(Au₂dppf)]ClO₄ (L = CH₂PPh₃, PPh₃, PPh₂Me), the tetranuclear complexes [S(AuL)₂(Au₂dppf)](ClO₄)₂ (L = PPh₃, PPh₂Me (**8**)), and the hexanuclear complex [(μ-Au₂dppf){S(Au₂dppf)}₂](OTf)₂ (**9**), in which two SAu₃ units are linked by the dppf ligands (18). The coordination sphere of the sulfur atom in **8** can be regarded as a trigonal bipyramid with one of the apical positions occupied by the lone pair of electrons and the other by the gold atoms. The complex is electron-deficient, however, since only three bonding molecular orbitals are occupied (19, 20). All these complexes display short gold-gold interactions. The reactions of [S(Au₂dppf)] with the gold(III) precursors [Au(C₆F₅)₃(OEt₂)] or [Au(C₆F₅)₂(OEt₂)₂]OTf afford mixed-valence complexes [S(Au₂dppf){Au(C₆F₅)₃}₂], [S(Au₂dppf){Au(C₆F₅)₃}] (**10**), and [(S(Au₂dppf))₂{Au(C₆F₅)₂}]OTf respectively (21, 22). The last two compounds show short gold(I)-gold(III) contacts (3.2195(8)-3.404(1) Å) which have been studied by theoretical calculations (22).

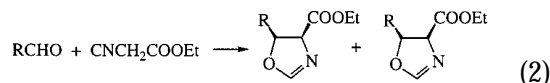
Analogous complexes have been prepared with E = selenium. The reaction of [(dppf)(AuCl)₂] with SeC(NH₂)₂, followed by basic hydrolysis, leads to [Se(Au₂dppf)] (**7**) (Box 3), which further reacts with [Au(C₆F₅)₃(OEt₂)] to give [Se(Au₂dppf){Au(C₆F₅)₃}] (**10**). The product shows weak gold(I)-gold(III) interaction as indicated by a short Au(I)⋯Au(III) distance of 3.541(1) Å (23).

Gold(III) complexes of the types [(dppf){Au(C₆F₅)₃}], [(dppf){Au(C₆F₅)₃}₂] and



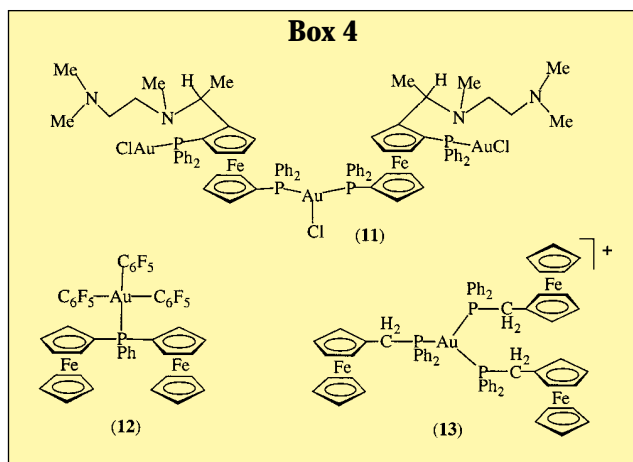
[(dppf){Au(C₆F₅)₂}]ClO₄ have been obtained by displacement of tht in [Au(C₆F₅)₃tht] or [Au(C₆F₅)₂(tht)₂]ClO₄ by the dppf ligand (**8a**).

The chiral aminoferrocenyldiphosphine [Fe(C₆H₄PPh₂){C₆H₃(PPh₂)-(CHMeNMeCH₂CH₂NMe₂)}] reacts with [AuCl(SMe₂)] to give the trinuclear derivative, [{Fe(C₆H₄PPh₂){C₆H₃(PPh₂)(CHMeNMeCH₂CH₂NMe₂)}₂](AuCl)₃ (**11**) (Box 4), which is an active catalyst for the enantioselective coupling of isocyanacetate esters with aldehydes, to form dihydrooxazoles (Equation 2) (24):



Diferrocenylphenylphosphine (PFc₂Ph) [Fc = (C₅H₅)Fe(C₅H₄)] reacts with gold(I) derivatives to afford the neutral or cationic complexes, [AuX(PFc₂Ph)] (X = Cl, C₆F₅) and [Au(PFc₂Ph)(PR₃)₂]ClO₄ (PR₃ = PFc₂Ph, PPh₃) (**25**). Ethynyl-gold(I) complexes, such as [(PhFc₂P)AuC≡CAu(PFc₂Ph)] and [(PhC≡CAu(PFc₂Ph))], are obtained by the reaction of [AuCl(PFc₂Ph)] with alkaline solutions of the corresponding ethyne (**26**). None of these compounds have short intermolecular metal-metal contacts in solid state structure (25-27). Reaction of PFc₂Ph with [Au(C₆F₅)₃(OEt₂)] and [Au(C₆F₅)₂Cl]₂ gives the gold(III) complexes [Au(C₆F₅)₃(PFc₂Ph)] (**12**) and [Au(C₆F₅)₂Cl(PFc₂Ph)], respectively (25).

Other neutral or cationic gold(I) complexes, such as [AuX{P(CH₂Fc)Ph₂}] (X = Cl, C₆F₅), [Au{P(CH₂Fc)Ph₂}₂]OTf [L = P(CH₂Fc)Ph₂, PPh₃], [Au{P(CH₂Fc)Ph₂}₃]OTf (**13**) and [AuX{P(CH₂Fc)Ph₂}₂] have been obtained, starting from the monophosphine P(CH₂Fc)Ph₂ (**28**). No intermolecular gold-gold contacts have been found in the crystal structures of



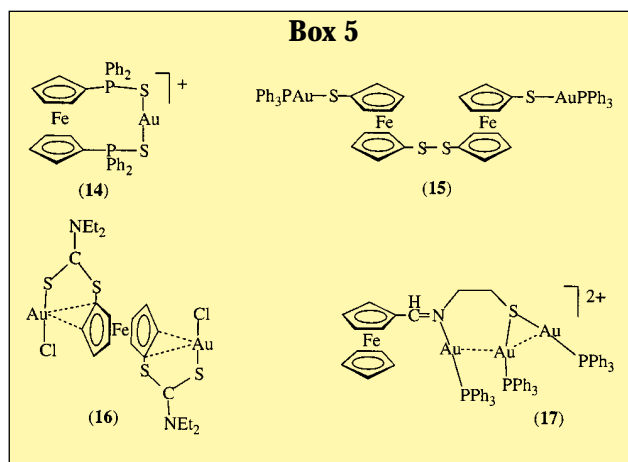
these compounds. The reaction of $\text{P}(\text{CH}_2\text{Fc})\text{Ph}_2$ with $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)]$ leads to $[\text{Au}(\text{C}_6\text{F}_5)_3\{\text{P}(\text{CH}_2\text{Fc})\text{Ph}_2\}]$ (28). With the hydroxymethylphosphine $\text{P}(\text{CH}_2\text{Fc})(\text{CH}_2\text{OH})_2$ the linear two-coordinate complex $[\text{Au}\{\text{P}(\text{CH}_2\text{Fc})(\text{CH}_2\text{OH})_2\}_2]\text{Cl}$ has been described (29).

COMPLEXES WITH S-SUBSTITUTED FERROCENE LIGANDS

The oxidation of dppf with sulfur to give 1,1'-bis(diphenylthiophosphoryl)ferrocene (dptpf), a ligand with a longer and more flexible skeleton. The reaction of dptpf with $[\text{Au}(\text{tht})_2]\text{OTf}$ in a 1:1 molar ratio leads to the complex $[\text{Au}(\text{dptpf})]\text{OTf}$ (14) (Box 5) with the dptpf acting as a *trans*-chelating ligand (30). The crystal structure reveals a linear coordination geometry at the metal centre for this complex and its silver analogue. Three- and four-coordinate complexes have been obtained with this ligand for silver, but not for gold (31).

The reaction of 1,1'-dithiolferrocene, $[\text{Fe}(\text{C}_5\text{H}_4\text{SH})_2]$, with $[\text{O}(\text{AuPPh}_3)_3]\text{BF}_4$ gives the dinuclear complex $[\text{Ph}_3\text{PAu}(\text{SC}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4\text{S}-\text{SC}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4\text{S})\text{AuPPh}_3]$ (15), as the product of an oxidative coupling of the ligand (32).

1,1'-Bis(diethylthiocarbamato)ferrocene, $[\text{Fe}(\text{C}_5\text{H}_4\text{S}_2\text{CNET}_2)_2]$, is another S-donor derivative with interesting ligand properties. It reacts with appropriate gold(I) or gold(III) precursors to give dinuclear complexes such as $[\text{Fe}(\text{C}_5\text{H}_4\text{S}_2\text{CNET}_2)_2(\text{AuCl})_2]$ (16), $[\text{Fe}(\text{C}_5\text{H}_4\text{S}_2\text{CNET}_2)_2(\text{AuPPh}_3)_2](\text{OTf})_2$, $[\text{Fe}(\text{C}_5\text{H}_4\text{S}_2\text{CNET}_2)_2\{\text{Au}(\text{C}_6\text{F}_5)_3\}_2]$, and $[\text{Fe}(\text{C}_5\text{H}_4\text{S}_2\text{CNET}_2)_2\{\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}\}_2]$ (33). The crystal structure analysis of 16 reveals a new type of η^2 -interaction between the gold centres and the



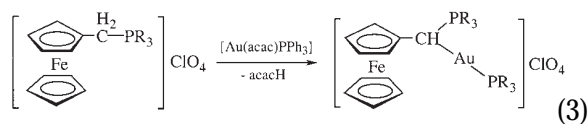
cyclopentadienyl rings, suggesting carbon-to-gold electron donation, in agreement with theoretical calculations (33). A similar situation may exist in the polymeric complex $[\text{Fe}(\text{C}_5\text{H}_4\text{S}_2\text{CNET}_2)_2\text{Ag}]_n(\text{ClO}_4)_n$ (34).

The condensation reaction of ferrocenecarbaldehyde with β -mercaptoethylamine gives $\text{FcCHN}(\text{CH}_2)_2\text{SH}$, which reacts with $[\text{AuCl}(\text{PPh}_3)]$ in the presence of Na_2CO_3 to afford the thiolate complex $[\text{FcCHN}(\text{CH}_2)_2\text{S}(\text{AuPPh}_3)]$. Further reaction of the latter in various molar ratios with $[\text{Au}(\text{OTf})\text{PPh}_3]$ leads to $[\text{FcCHN}(\text{CH}_2)_2\text{S}(\text{AuPPh}_3)_2]\text{OTf}$, $[\text{FcCHN}(\text{AuPPh}_3)(\text{CH}_2)_2\text{S}(\text{AuPPh}_3)_2](\text{OTf})_2$ (17) and $[\text{FcCHN}(\text{AuPPh}_3)(\text{CH}_2)_2\text{S}(\text{AuPPh}_3)_3](\text{OTf})_3$, in which the gold centres are coordinated to the sulfur and nitrogen atoms (35). Complex 17 shows short $\text{Au}\cdots\text{Au}$ interactions for all three metal centres. The cyclic voltammograms (35) show a quasi-reversible redox couple assigned to ferrocene/ferrocenium species at potential values similar to those found in ferrocene itself. A small irreversible wave appears at higher potential (*ca* 0.8 V), probably due to an amine oxidation process. This signal is absent for complexes with an $[\text{AuPPh}_3]^+$ unit on the nitrogen atom.

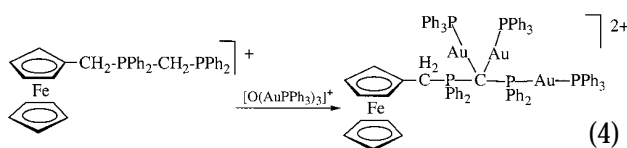
COMPLEXES WITH C-FUNCTIONAL FERROCENE LIGANDS

Phosphonium salts of the types $[\text{FcCH}_2\text{PR}_3]\text{ClO}_4$ ($\text{PR}_3 = \text{PPh}_3, \text{PPh}_2\text{Me}$) and $[\text{FcCH}_2\text{PPh}_2\text{CH}_2\text{PPh}_2]\text{X}$ ($\text{X} = \text{ClO}_4, \text{OTf}$), obtained by reaction of $[\text{FcCH}_2\text{NMe}_3]\text{I}$ with tertiary or ditertiary phosphines, can act as precursors for C-donor ligands in gold chemistry. Thus, the treatment of $[\text{FcCH}_2\text{PR}_3]\text{ClO}_4$ with $[\text{Au}(\text{acac})(\text{PPh}_3)]$ leads to the ylide complexes

[FcCH(AuPPh₃)PR₃][ClO₄], derived from substitution of one proton of the methylene group by the [Au(PPh₃)]⁺ unit (Equation 3):



The oxonium salt [O(AuPPh₃)₃][ClO₄] can also act as deprotonating agent and reacts with [FcCH₂PPh₂CH₂PPh₂][ClO₄] to give the trinuclear methanide complex [FcCH₂PPh₂C(AuPPh₃)₂PPh₂(AuPPh₃)](ClO₄)₂ (Equation 4) (36):



CONCLUSIONS

Ferrocene is a versatile building block for the synthesis of ligands and complexes having interesting chemical and physical properties. One of the more important features is the flexibility of the bidentate ligands which permits the formation of gold(I) and gold(III) complexes with a number of different structural frameworks. These ferrocene derivatives can act as (a) bridging ligands in di- or polynuclear derivatives, (b) as chelating agents in gold(III) or three-coordinate gold(I) compounds, and (c) through a new type of η²-interaction between the gold centre and the cyclopentadienyl ring.

The coordination chemistry of gold is currently attracting growing interest, arising both from the novel structures of the gold complexes and their potential applications. Their potential use as anti-tumour agents is being investigated. Ferrocene/ferrocenium couples could find use in biosensors and chiral ferrocene derivatives have potential in catalysis. Other application areas could include use in the synthesis of materials for second- and third-order non-linear optical effects, magnetic materials and ferrocene-based polymers.

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Continued from page 89

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