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Anionic iron clusters as building blocks for the synthesis of higher nuclearity compounds containing 11- and 12-group elements

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Abstract

Anionic iron clusters have been widely used as building blocks for the formation of mixed metal clusters with 11- and 12- group elements. This review summarizes the results reported in this area, paying special attention to the structural features of the metal core of the species reported.

Keywords: Transition metal clusters; Building blocks; Iron carbonyl anions; 11-Group elements; 12-Group elements

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1. Introduction

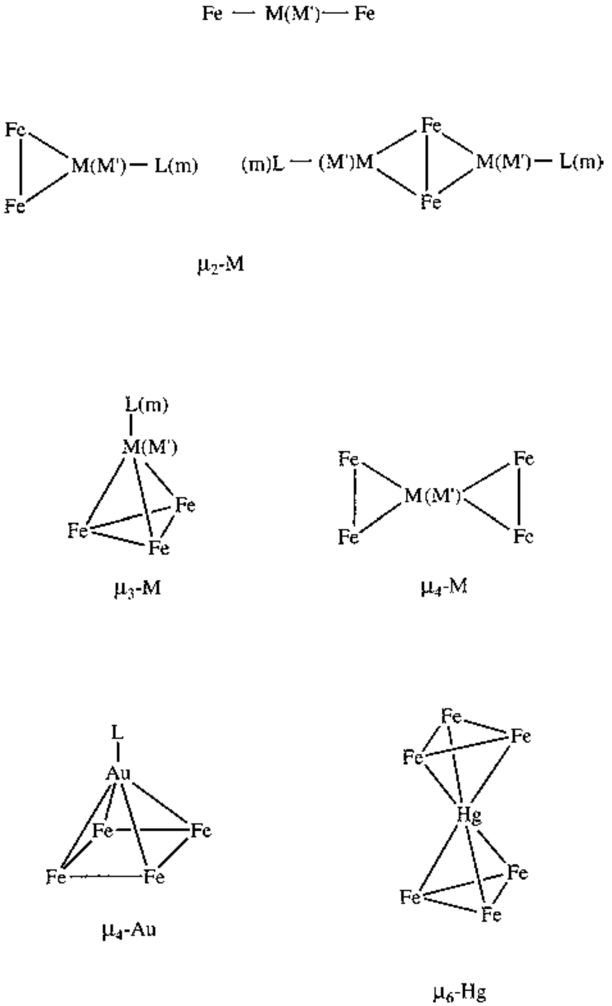
Although transition metal compounds containing bonds to 11- and 12-group elements have been known for a long time, it was not until the early 1980s that a rapid expansion of the chemistry of this class of compounds occurred. This is because the ability of 11- and 12-group elements, particularly gold and mercury, to form multicenter metal–metal bonds has allowed the synthesis of fascinating structures which have been established by X-ray crystallography. Moreover high-nuclearity clusters containing up to a few dozen metal atoms has led to an increased interest in their chemical and physicochemical properties.

Most of the currently known heteronuclear cluster compounds containing ML^+ ($M = Cu$, Ag, Au; $L =$ phosphine ligand) or M' (X or m)$^+$ ($M' = Zn$, Cd, Hg; $X =$ halide, $m =$ metal fragment, such as $Mo(CO)_3Cp$) moieties have been obtained by treating an anionic metal cluster with one or more ML or M′(X or m) units. Usually, the resulting compound is a neutral or an anionic cluster.

The success of this method depends on a number of factors, the most important being the availability of the anionic metal cluster. In the chemistry of iron the following cluster anions have been used as building blocks [1]: di- and tri-iron cluster anions, such as $[Fe_2(CO)_8]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$ and related bridged species; the tetranuclear anions $[Fe_4(CO)_{13}]^{2-}$ and $[Fe_4C(CO)_{12}]^{2-}$ and similar heteronuclear derivatives, such as $[HFe_4(CO)_{12}BH]^-$ or $[Fe_4N(CO)_{12}]^-$; the penta-iron compound $[Fe_5C(CO)_{14}]^{2-}$ and the hexanuclear anion $[Fe_6C(CO)_{16}]^{2-}$.

Iron cluster anions with a nuclearity higher than six have not been described so far. On the other hand, there are a number a mixed transition-metal iron clusters which have been prepared and used as building blocks for the synthesis of clusters containing 11- and 12-group elements, but they are not discussed in this article.

An interesting point related to this topic concerns the bonding mode exhibited for ML^+ or M' (X or m)$^+$ fragments in their attachment to the iron polyhedra. Chart 1 shows those more frequently found. In general, the two-centre-two-electron bonding mode is observed only for the simplest bi- or tri-metallic compounds. Typical μ_2- and μ_3- bonds are found for a large number of iron clusters in which the ML^+ or M' (X or m)$^+$ unit bridges metal–metal edges or caps triangular faces of cluster cores, respectively. In most of μ_4 11- and 12-group elements the metal bridges two edges of two identical cluster moieties containing two or more metal atoms each. Five-center bond (μ_4-M) and two four-centre-two electron bonds (μ_6-M), are only found for gold or copper and mercury complexes, respectively (Chart 1).



μ_2-M

μ_3-M

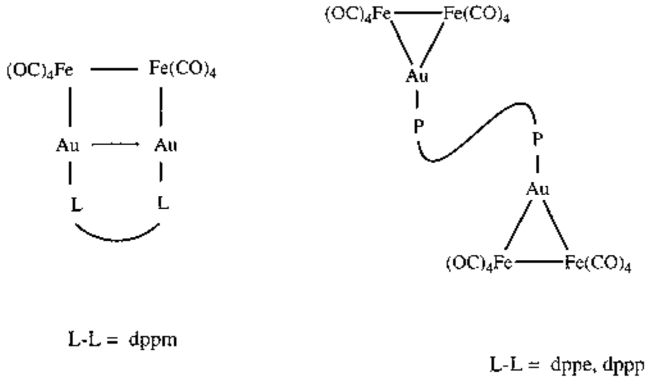
μ_4-M

μ_4-Au

μ_6-Hg

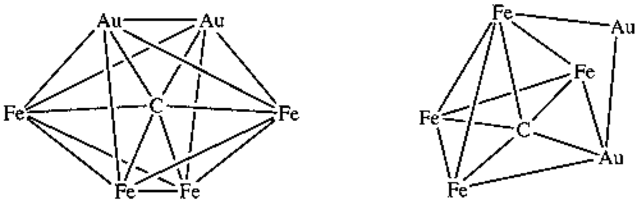
(Chart 1)

The results obtained by using $[M_2(\mu\text{-}L)]^{2+}$ or $[M_3(\mu\text{-}L)]^{3+}$ moieties (M = Au, Cu; L = polyphosphine ligand) instead of ML^+ are of particular interest. They can be incorporated into the structure of the metal precursor, increasing its nuclearity by two or three units, respectively. Alternatively, they can bridge two or three metal clusters, by attaching to them through only one M atom (Chart 2). It has been reported that the nature of the final cluster depends dramatically on the bite angle of the diphosphine ligand [2].



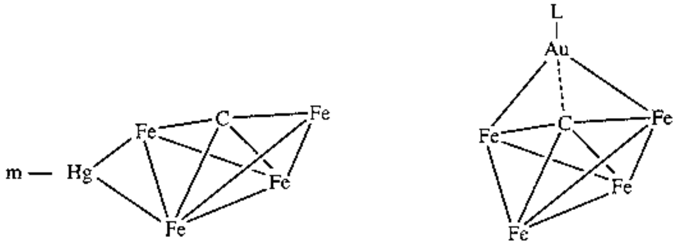
(Chart)

In addition, the rigidity of the $[Au_2(\mu\text{-}L)]^{2+}$ unit may lead to a cluster compound containing a different metal core from that obtained using two moles of $AuPR_3^+$. For example, $[Fe_4C(CO)_{12}(AuPEt_3)_2]$ [3] and $[Fe_4C(CO)_{12}\{Au_2(dppm)\}]$ (dppm = bis(diphenylphosphino)methane) [4] have different geometry in the solid state and, consequently, exhibit skeletal isomerism (Chart 3).



(Chart 3)

It is remarkable that despite the fact that $AuPR_3^+$ and Hgm^+ are isolobal species they show different sites of attachment to $[Fe_4C(CO)_{12}]^{2-}$. Thus, while a mercury atom bridges one of the two edges defined by wingtip and hinge iron atoms of the Fe_4C butterfly, the gold atom overbridges the butterfly [5] (Chart 4).



(Chart 4)

Although excellent reviews of transition-metal clusters containing 11 and 12-group elements have appeared [6,7], here we discuss the specific use of iron cluster anions as building blocks to form such compounds, and the skeletal metal core of the resulting clusters is discussed according to the nature of the incoming groups. We provide examples from the literature up to mid-1998.

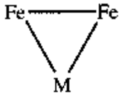
2. Dinuclear anionic iron clusters as building blocks.

Dinuclear anionic iron compounds may take on a dinegative unbridged form, $[Fe_2(CO)_8]^{2-}$ or the mononegative bridged form $[Fe_2(\mu\text{-}Z)(CO)_7]^-$ (Z = a 3-electron donor group).

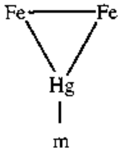
First we will describe the use of the dianionic species as a building block for the synthesis of mixed metal clusters and then the use of the mononegative species in the same type of reaction.

2.1. Di-negative iron anions

The high nucleophilicity of $[Fe_2(CO)_8]^{2-}$ facilitates the reaction with 1 mole of $MPPh_3^+$ (M = Au [8], Cu, Ag [9]) or Hgm^+ (m = a metal fragment, such as $Mo(CO)_3Cp$, $Mn(CO)_5$, etc.) [10] to give a triangular metal complex (structural type **I**) or an spiked triangular metal skeleton (**II**), respectively. The silver compound is the least stable of them and it can not be isolated in solid state.

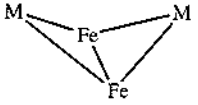


I



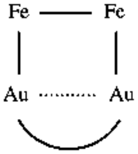
II

Attempts to incorporate a new metal unit in the structures **I** or **II** are rarely successful. Thus, the use of an excess of $ClMPPh_3$ or ClHgm did not result in the formation of either tetra or hexametallic clusters respectively and the starting materials were recovered. However, the substitution of the PPh_3 ligand by other phosphines with different electronic and steric characteristics such as PCy_3 or P^tBu_3, allowed the synthesis of neutral compounds with formula $[Fe_2(CO)_8(MPR_3)_2]$ [11,12] which contain an Fe_2Cu_2 butterfly metal core with the Fe–Fe single bond doubly bridged by two $CuPR_3^+$ fragments (**III**).

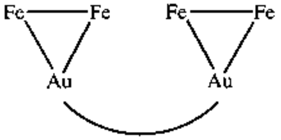


III

Another strategy makes use of the compounds $(ClAu)_2(L\text{–}L)$ as a source of group 11 metals. The reaction between $[Fe_2(CO)_8]^{2-}$ and one equivalent of $(ClAu)_2(L\text{–}L)$ (L–L = dppm) gave a cluster with a nearly square tetrametal core (**IV**) as confirmed by X-ray analysis [2]. In the case of L–L = dppe (bis-diphenylphosphino)ethane) or dppp (bis(diphenylphosphino)propane), addition of another equivalent of the iron anion produced hexanuclear anions of the type $[\{Fe_2(CO)_6(\mu\text{-}CO)_2Au\}_2(\mu\text{-}L\text{–}L)]^{2-}$ (**V**). This transformation was reversed by addition of more of the phosphine gold halide.



IV

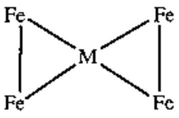


V

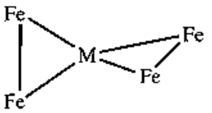
Other example of the last structural type was prepared by adding the appropriate amounts of $[Cu(CH_3CN)_4]PF_6$ and $Cy_2PCH_2CH_2PCy_2$ to a solution of $[Fe_2(CO)_8]^{2-}$ yielding the hexanuclear compound $[PPh_4][\{Fe_2(CO)_8Cu\}_2(\mu\text{-}Cy_2PCH_2CH_2PCy_2)]$ where all the CO ligands are terminally bonded [11].

The use of $(ClAu)_3$(triphos) as a source of gold fragments did not provide a cluster with a planar Fe_2Au_2 framework. Independently of the molar ratios the only cluster formed was the highly unstable nonanuclear trianion $[\{Fe_2(CO)_6(\mu\text{-}CO)_2Au\}_3(\mu_3\text{-triphos})]^{3-}$ [13] probably due to the large bite angle of the triphos ligand.

$[Fe_2(CO)_8]^{2-}$ has also been used to obtain Fe/M or M′ (M = Au, M′ = Cd, Hg) clusters containing M or M′ exclusively coordinated by metals. The monoanionic compound $[Fe_4Au(CO)_{16}]^-$ [14] was obtained by reaction of $[Fe_2(CO)_8]^{2-}$ with $[AuCl_4]^-$ or $ClAu(SEt_4)$ (alternatively mononuclear $[Fe(CO)_4]^{2-}$ or trinuclear $[Fe_3(CO)_{11}]^{2-}$ could be used as iron source being the latter that provide the highest yields). This anion displays a bow-tie pentametallic structure (**VI**) and can be described in terms of two $[Fe_2(CO)_8]^{2-}$ anions linked to a central gold (III) atom adopting a square-planar coordination. In contrast, although no structural data are available for the $[Fe_4M'(CO)_{16}]^{2-}$ (M′ = Cd, Hg) dianions, it is believed that in these spiro clusters M’ essentially exhibits a tetrahedral geometry (**VII**) [14].



VI



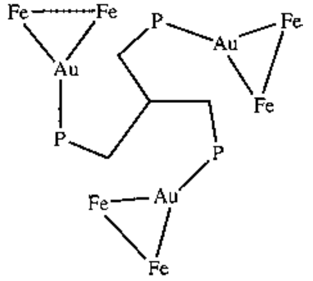
VII

2.2. Mono-negative iron anions

Dinuclear anions of formula $[Fe_2(CO)_7(\mu\text{–}Z)]^-$, are the most widely used. In most cases, the presence on these of only one negative charge limits the possibility of incorporation of group 11 and 12 metal fragments to one.

On the other hand, bridging ligands usually provide greater stability since they inhibit the fragmentation of the clusters formed. For example, the reaction of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}Z)]^-$ ($Z = PPh_2$, P^tBu_2, RCCRH {R = Ph, H}) with $MPPh_3^+$ gave of the neutral triangular metal clusters $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}Z)(\mu\text{-}MPPh_3)]$ ($Z = PPh_2$ [9], P^tBu_2 [15], M = Cu, Ag, Au; Z = RCCRH {R = Ph, H} [16], M = Au) (**I**). Similar derivatives, showing a spiked triangular metal core (**II**), were prepared by the action of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ on the mercury derivatives ClHgm (m = CpMo$(CO)_3$, CpW$(CO)_3$, $Co(CO)_4$, $Mn(CO)_5$, CpFe$(CO)_2$). The neutral species $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}Hgm\}]$ [10] spontaneously redistributed to the spiro-type complex $[Hg\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$ and Hgm_2, in contrast with the behaviour of the related negative species $[Fe_2(CO)_8\{\mu\text{-}Hgm\}]^-$, which are stable towards the symmetrization process. This is because this process proceeds through an associative mechanism which operates less efficiently with charged species.

The reaction of $(ClAu)_2(L\text{–}L)$ [16,17] (L–L = dppm, dppip (bis(diphenylphosphino)isopropane), dppe, dppp) or $(ClAu)_3$(triphos) (triphos = 1,1,1-tris-(diphenylphosphinomethyl)ethane) [13] and two or three equivalents of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}Z)]^-$ ($Z = PPh_2$, P^tBu_2, R′CCRH {R = R′ = Ph, H; R′ = H, R = Ph}), respectively, gave species in which two or three Fe_2Au triangular cluster units are linked by the polyphosphine ligand (structural types **V** and **VIII**, respectively). The determination of the molecular structure of one type **VIII** compound showed that the disposition of the $CH_3C(CH_2PPh_2Au)_3$ fragment differs from both the free phosphine and the trigold derivative $CH_3C(CH_2PPh_2AuCl)_3$, the local symmetry being approximately C_3, with a propeller-like arrangement.



VIII

In the case of the thiolate iron anions $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}SR)]^-$ [18] the process appeared to be more complicated and chromatographic workup was necessary in order to isolate in moderate yields the iron-gold clusters from mixtures of different products whose nature was shown to depend on the R group. For R = ^{i}Pr, ^{t}Bu and Ph the mixed iron-gold clusters with triangular skeletons were obtained. In contrast, no mixed iron-gold clusters were obtained for R = Et, C_6F_5 and phosphine mono or disubstituted di-iron complexes were isolated instead.

Analogously, the reaction between the anion $[Fe_2(CO)_6(\eta^2, \mu\text{-}C_{11}H_{19}S)]^-$ and the gold-phosphine fragment gave the compound $[Fe_2(CO)_6(\eta^2, \mu\text{-}C_{11}H_{19}S)(\mu\text{-}AuPPh_3)]$ [19].

The basic skeleton of all these clusters consists of an Fe_2M triangle where the Fe–Fe bond appears bridged by either two different ligands or a group with two coordination sites.

Occasionally, neutral dinuclear species have been used as building blocks for the formation of higher nuclearity clusters. As an example, the addition of silver salts AgX ($X = ClO_4^-$, PF_6^-) to the iron–iron bond of the μ-alkylidene complexes $[Fe_2(CO)_6\{CHCPh(NRR')\}\ (\mu\text{-}PPh_2)]$ ($R = H$, $R' = CH_3$, C_2H_5, $CH(CH_3)_2$, c-C_6H_{11}; $R = R' = C_2H_5$) affords the mixed triangular clusters $[Fe_2Ag(CO)_6\{CHCPh(NRR')\}(\mu\text{-}PPh_2)]X$ [20]. In spite of the lack of negative charges on the iron building block, spectroscopic data suggest that the Fe–Fe bonds in these compounds are exceptionally electron rich their behaviour being similar to that of the cluster anions described.

A neutral iron/mercury spiro cluster (**VI**) has been reported from the reaction between $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ and $Hg(CN)_2$ [10]. Other examples of spiro clusters, $[Hg\{Fe_2(CO)_6(\mu\text{-}SR)(\mu\text{-}CH_3OCH_2CHC)\}]$ ($R = {}^tBu$, Et) [21] were found together with other products and after chromatographic work up from the reaction of the anion $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}SR)]^-$ and the dialkynylmercury derivative $Hg(CCCH_2OCH_3)_2$. A multistep process seems to be responsible for the formation of these compounds.

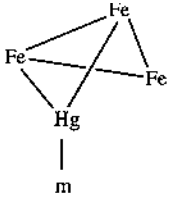
3. Trinuclear anionic iron clusters as building blocks

3.1. Di-negative iron anions

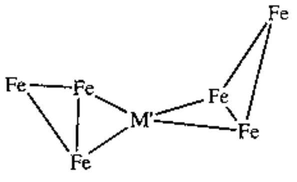
$[Fe_3(CO)_{11}]^{2-}$ is the most widely used di-negative tri-iron anion and it has been reacted with both gold and mercury derivatives.

The reaction between the trimetallic iron anion $[Fe_3(CO)_{11}]^{2-}$ and $ClAuPR_3$ ($R =$ Ph, CH_3) in a 1:1 molar ratio gave the tetrametallic anionic cluster $[Fe_3(CO)_{11}(\mu\text{-}AuPR_3)]^-$ [22]. The metal core consists of an Fe_3Au butterfly arrangement (**III**) in which the $AuPR_3$ fragment bridges one edge of the Fe_3 triangle. Efforts to increase the nuclearity of the latter by adding an excess of gold complex were unsuccessful. The reaction of the iron dianion with the polygold derivatives $(ClAu)_2(L\text{–}L)$ [22] or $(ClAu)_3$(triphos) [23] led only to compounds containing independent tetrametallic clusters and, in contrast with the results described for the $[Fe_2(CO)_8]^{2-}$ and $(ClAu)_2(L\text{–}L)$ (L–L = dppm, dppe), the expected pentametallic species were not obtained.

Likewise, $[Fe_3(CO)_{11}]^{2-}$ displaced a chlorine atom from ClHgm to afford the anionic spiked butterfly clusters $[Fe_3(CO)_{11}\{\mu\text{-}Hgm\}]^-$ (m = $Mo(CO)_3Cp$, $W(CO)_3Cp$ $Fe(CO)_2Cp$, $Mn(CO)_5$, $Co(CO)_4$) [24] (**IX**).



IX



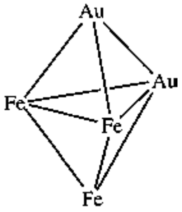
X

The symmetric spirocyclic heptametallic clusters $[M'\{Fe_3(CO)_{11}\}_2]^{2-}$ ($M' = Cd$, Hg) [25] (**X**) were obtained when either $[Fe_3(CO)_{11}]^{2-}$ or $[Fe_4(CO)_{13}]^{2-}$ was treated with CdI_2 or $HgBr_2$. The structure of the cadmium derivative shows the coordination of two Fe_3 units to a central cadmium atom, which is surrounded by four iron atoms in a rather distorted spiro-type coordination. Upon varying the molar ratio of the reagents the butterfly anionic cluster $[Fe_3(CO)_{11}(\mu\text{-}HgBr)]^-$ was also obtained.

The use of other dianion building blocks provides a wider range of metal core structures as a result of the cluster expansion. The reaction of $[Cu(CH_3CN)_4]^+$ and $[Fe_3(CO)_9(\mu_3\text{-}CCO)]^{2-}$ followed by addition of I^- in a 1:1:1 molar ratio produced the ketenylidene butterfly cluster $[Fe_3(CO)_9(\mu_3\text{-}CCO)(CuI)]^{2-}$ [26], in which the fragment CuI occupies a wingtip position of the butterfly core. Cu^+/iron anion beyond 1:1 suggested the possible incorporation of a second copper unit but this complex could not be isolated since its limited stability.

The pentanuclear $[Fe_3(CO)_9(\mu_3\text{-}CCO)(AuPPh_3)_2]$ [27] was formed by using two equivalents of the gold fragment $AuPPh_3^+$. Two geometries of the metal core are proposed on the basis of the NMR data for this compound, since no crystal structure has been carried out.

The reaction of $[Fe_3(CO)_9(\mu_3\text{-}E)]^{2-}$ (E = O [28], S [29]) and $AuPPh_3^+$ in a 1:2 molar ratio gave the neutral compounds $[Fe_3(CO)_9(\mu_3\text{-}E)(AuPPh_3)_2]$. The metal core of these clusters consists of a M_3Au_2 trigonal-bipyramidal framework in which the two gold atoms are located in an axial and an equatorial position respectively (**XI**).



XI

Closely related derivatives of copper and silver have also been described [30]. These are obtained in low yields together with the monosubstituted hydrido compounds $[HFe_3(CO)_9(\mu_3\text{-}S)(MPR_3)_2]$ (M = Cu, Ag, R = Ph, CH_3).

Curiously, the addition of two gold fragments to the related anion $[Fe_3(CO)_9(\mu_3\text{-}Te)]^{2-}$ led to decomposition products whereas a clean reaction was observed for a 1:1 molar ratio giving the monoanionic butterfly trimetallic cluster $[Fe_3(CO)_9(\mu_3\text{-}Te)(AuPPh_3)]^-$ [31]. The reaction of the anion with CuCl allowed the isolation of the copper butterfly adduct $[Fe_3(CO)_9(\mu_3\text{-}Te)(CuCl)]^{2-}$ [32]. Substitution of CuCl by $ClCuPEt_3$ was observed to accelerate the process rate but the outcome remained unchanged. The reaction between the anion $[Fe_3(CO)_9(\mu_3\text{-}Te)]^{2-}$ and the asymmetric mercury salt PhHgOAc in a molar 1:1 molar ratio gave the tetrametallic cluster $[Fe_3(CO)_9(\mu_3\text{-}Te)(\mu\text{-}HgPh)]^-$ [31]. No crystal structure was obtained for this product; however, the IR solution of the CO region is nearly superimposable with that of the analogous gold derivative, suggesting a butterfly metal core geometry.

The use of various symmetric mercury salts gave rise to clusters with different structural features. Whereas the reaction between the tetrahedral cluster $[Fe_3(CO)_9(\mu_3\text{-Se})]^{2-}$ and the mercury salt HgI_2 formed the μ-Hg cluster $[Fe_3(CO)_9(\mu_3\text{-Se})(\mu\text{-HgI})]^-$ [33] (**III**), the treatment with $Hg(OAc)_2$ yielded the μ_4-Hg spiro-type heptanuclear anion $[Hg\{Fe_3(CO)_9(\mu_3\text{-Se})\}_2]^{2-}$ [34] (**X**).

Reactions of the bridged phosphorus anions $[Fe_3(CO)_9(\mu_3\text{-PR})]^{2-}$ with copper and gold phosphine halides lead to cluster expansion and the trigonal-bipyramidal pentametallic clusters $[Fe_3(CO)_9(\mu_3\text{-PR})(MPR'_3)_2]$ (R = Ph, R′ = Ph, Tol, M = Au; R = CH_3, Ph, R′ = Ph, Tol, M = Cu) (**XI**) are obtained. Silver phosphine halides form two compounds of unknown structure with two phosphine ligands per silver atom $[HFe_3(CO)_9(\mu_3\text{-PPh})\{Ag(PPh_3)_2\}]$ and $[Fe_3(CO)_9(\mu_3\text{-PPh})\{Ag(PPh_3)_2\}_2]$ [35].

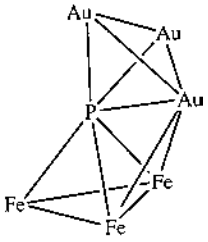
3.2. Mono-negative iron anions

The reaction between the monocharged iron anion $[Fe_3(CO)_9(\mu_3\text{-HCN}^t\text{Bu})]^-$ and $AuPPh_3^+$ produced the neutral compound $[Fe_3(CO)_9(\mu_3\text{-HCN}^t\text{Bu})(AuPPh_3)]$ [36]. The complex contains an $AuFe_3$ butterfly skeleton.

The use of the related anions $[Fe_3(CO)_{10}(\mu_3\text{-CR})]^-$ yielded analogous butterfly mixed clusters $[Fe_3(CO)_9(\mu_3\text{-CO})(\mu_3\text{-CR})(MPPh_3)]$ (R = CH_3, M = Au, Cu [37]; R = C_3H_5, M = Au [27]; R = OCH_3, M = Cu, Ag, Au [38]).

For the thiolate bridged compounds $[Fe_3(CO)_9(\mu_3\text{-SR})]^-$ (R = ^{i}Pr, ^{t}Bu, C_6H_{11}, Et) different yields (10 up to 85%) of the neutral tetrametallic butterfly clusters $[Fe_3(CO)_9(\mu_3\text{-SR})(AuPPh_3)]$ were obtained as a function of the R group after chromatographic work-up [39].

A different reaction pattern was observed when $[HFe_3(CO)_9(\mu_3\text{-PH})]^-$ was treated with $ClAuPR_3$ [40]. The primary site of interaction is the terminal hydride on the phosphorus heteroatom and, thus, the clusters $[HFe_3(CO)_9\{P(AuPR_3)_2\}]$ (R = Ph, Et) were accessible by reaction of two equivalents of $AuPPh_3^+$ with the starting iron cluster. Asymmetric Au_2 clusters with two different phosphine ligands bound to the gold atoms were prepared by exchange reaction between two different symmetric Au_2 clusters. The addition of three equivalents of the gold compound allowed the obtention of the hexametallic $[Fe_3(CO)_9\{P(AuPR_3)_3\}]$, whose structure can be understood as consisting of an $[Fe_3(CO)_9(\mu_3\text{-P})]^{3-}$ cluster framework coordinated to a Au–Au bonded triangular $[(AuPR_3)_3]^{3+}$ unit (**XII**).



XII

4. Tetranuclear anionic iron clusters as building blocks

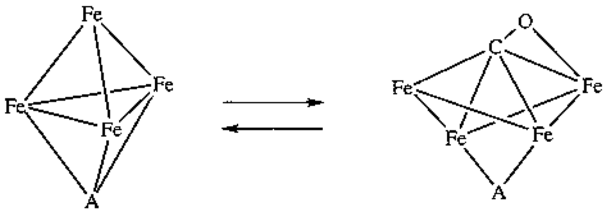
4.1. Di-negative iron anions

Two dinegative tetranuclear iron clusters have been used as building blocks for the synthesis of higher nuclearity mixed metal clusters: $[Fe_4(CO)_{13}]^{2-}$ and $[Fe_4C(CO)_{12}]^{2-}$.

The $[Fe_4(CO)_{13}]^{2-}$ anion is particularly interesting. Its X-ray crystal structure determination established that the metal core consists of a tetrahedral array of iron atoms [41], but its protonated derivative $[Fe_4(CO)_{13}H]^-$ contains a butterfly array of iron atoms with a Π-CO group [42]. Subsequent variable-temperature multinuclear NMR spectroscopic studies indicated that $[Fe_4(CO)_{13}H]^-$ exists in solution as an equilibrium mixture of two isomers [43] (Scheme 1):

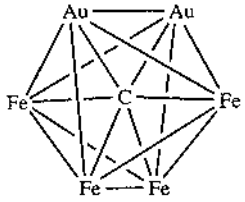
Analogous equilibria can be established when a variety of Lewis acids are used in place of the proton. Thus, the Lewis acid ligands $[HgCH_3]^+$, $AuPR_3^+$ and $CuPR_3^+$ interact with the metal framework of the tetrahedral iron cluster $[Fe_4(CO)_{13}]^{2-}$ to give two products [44]. One of which consists of the Fe_4 tetrahedron with the Lewis acid capping one face, and the other is a Fe_4 butterfly array with the Lewis acid ligand on the hinge and a Π-CO between the wingtips. By proper choice of counterion and conditions, either the butterfly or tetrahedral form can be crystallized. It is generally understood that butterfly formation is promoted by electronic factors such that the strongest acid produces the highest concentration of the butterfly isomer. However, a higher butterfly-to-tetrahedral isomer ratio was observed for solutions of $[PPN][Fe_4(CO)_{13}\{HgMo(CO)_3Cp\}]$ than for the $[Fe_4(CO)_{13}(HgCH_3)]^-$, which contains a less bulky Lewis acid ligand. Since the electron density on the cluster is not significantly altered by substituting $HgMo(CO)_3Cp^+$ for $HgCH_3^+$, according to the CO stretching frequencies, it was concluded that steric effects are the likely origin for the higher butterfly concentration in $[PPN][Fe_4(CO)_{13}\{HgMo(CO)_3Cp\}]$ [45].

$[Fe_4(CO)_{13}]^{2-}$ has been used as starting material for the preparation of $[Fe_4C(\mu\text{-}H)(CO)_{12}(AuPR_3)]$ and $[Fe_4C(CO)_{12}(AuPR_3)_2]$ ($R = Ph$, Et) [3]. The proposed mechanism is as follows: the reaction of the anion with $ClAuPR_3$ ($R = Ph$, Et) yields an anion which, upon protonation and oxidation of some of the cluster, gives the compound $[Fe_4C(\mu\text{-}H)(CO)_{12}(AuPR_3)]$. This complex is reversibly deprotonated in the presence of a base and the resultant anion, upon treatment with $ClAuPR_3$,



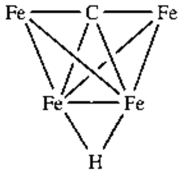
Scheme 1.

gives $[Fe_4C(CO)_{12}(AuPR_3)_2]$; the formation of the latter involves attack at the carbido centre by the gold phosphine group. The metal core of the di-gold derivative is represented by **XIII**.

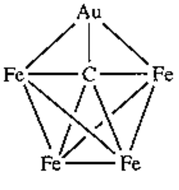


XIII

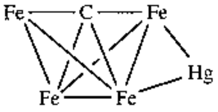
The nature of the final products of the reaction between Lewis acids and polynuclear metal anions is sometimes difficult to predict, particularly if the metal anions incorporate a p-block element at an exposed site. This is because the incoming metal ligand may interact with either the metal or the main group atom sites. The $[Fe_4C(CO)_{12}]^{2-}$ is an interesting example of this. The iron anion reacts with the species H^+ [46], $AuPPh_3^+$ [47] and $HgMo(CO)_3Cp^+$ [5] to give, unexpectedly, three skeletal isomers by bridging the hinge (**XIV**), by overbridging the butterfly (**XV**), or by bridging one of the two edges defined by the wingtip and hinge iron atoms (**XVI**), respectively. The different attachment of the three cationic species to the butterfly anion is remarkable if we consider that they are isolobal fragments, as shown in a large series of compounds. Steric requirements and the π overlap capacity of these fragments seem to be responsible for this different behaviour.



XIV



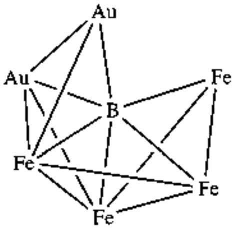
XV



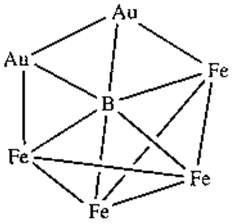
XVI

4.2. Mono-negative iron anions

The boron-containing anion $[HFe_4(CO)_{12}BH]^-$ has been widely used as starting material for the preparation of mixed iron-gold clusters. Its reaction with $ClAuPPh_3$ gives the metal-rich auraferraborane $[Fe_4(CO)_{12}BH(AuPPh_3)_2]$ [48]. This cluster has an unprecedented core structure consisting of a boron atom associated with an irregular array of four iron and two gold atoms. However, the Fe_4B butterfly geometry is retained. By varying the nature of the phosphine ligand, two new structural types were found [49]: one, very similar to that of $[Fe_4(CO)_{12}BH(AuPPh_3)_2]$, in which the endo hydrogen atom bridges an Fe–B edge (**XVII**), and the other in which the hydrogen atom bridges an Fe–Fe edge (**XVIII**). Unlike the structure **XVII**, **XVIII** possesses one C_2 axis passing through the boron atom and the centre of the hinge bond of the tetra-iron butterfly skeleton. A discussion of the factors leading to one or other structure has been carried out.



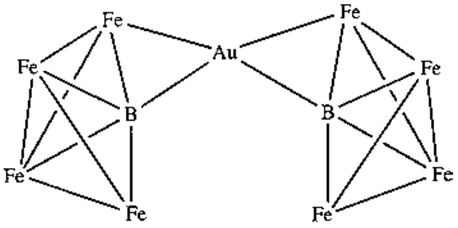
XVII



XVIII

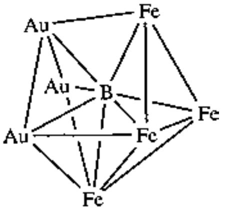
The compound $[Fe_4(CO)_{12}BH(AuAsPh_3)_2]$ is structurally similar to the PPh_3 derivative, although its redox chemistry is significantly different [50].

A product of the reaction of $[PPN][HFe_4(CO)_{12}BH]$ with either $ClAuPMe_2Ph$ or $ClAuPMePh_2$ is the cluster $[\{HFe_4(CO)_{12}BH\}_2Au][AuL_2]$ ($L = PMePh_2$ or PMe_2Ph), whose anion contains two tetra-iron butterfly, boron containing, fragments linked by a naked gold atom (**XIX**) [51].



XIX

Treatment of [PPN][$HFe_4(CO)_{12}BH$] with [$(PPh_3Au)_3O$][BF_4] yielded the first example of a structurally characterised cluster containing a naked boron atom, [$Fe_4(CO)_{12}B(AuPPh_3)_3$] [52]. In this, the boron atom is within bonding contact of all seven metal atoms (**XX**).



XX

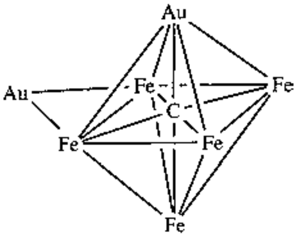
The reaction of [PPN][$HFe_4(CO)_{12}BH$] with $(ClAu)_2$(dppm) leads to a mixture of the borido cluster [$HFe_4(CO)_{12}B\{Au_2(dppm)\}$](major product) **(XVIII)** and the salt [PPN][$\{HFe_4(CO)_{12}BH\}_2Au$] (minor product)[53].

Other mono-negative tetra-iron anions have also been used as starting materials for mixed transition metal clusters. For example, [$Fe_4(CO)_{12}(COCH_3)(AuPEt_3)$] [54] and [$Fe_4N(CO)_{12}(AuPPh_3)$] [55] are prepared by reaction of [$Fe_4(CO)_{12}(COCH_3)$]$^-$ and [$Fe_4N(CO)_{12}$]$^-$ with the corresponding gold halide derivative. Interestingly, the first compound provides an example of a CO ligand formally acting as an overall six-electron donor ($4e^-$ to the cluster framework and $2e^-$ to the CH_3^+ group).

5. Pentanuclear anionic iron clusters as building blocks

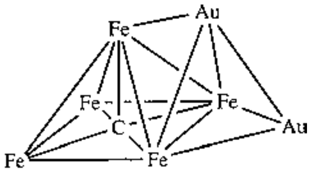
The penta-iron carbide anion, [$Fe_5C(CO)_{15}$]$^{2-}$, is a good nucleophile to form heteronuclear metal clusters with 11- or 12-group elements.

Thus, the reaction of the iron anion with $ClAuPEt_3$ in the presence of $TlPF_6$, as a halide abstractor, affords the anion [$Fe_5C(CO)_{15}(AuPEt_3)$]$^-$, not isolated, which in turn, reacts with an excess of the gold complex to give the neutral cluster [$Fe_5C(CO)_{15}(AuPEt_3)_2$] [56]. Its molecular structure is unusual in that it contains two $AuPEt_3$ groups which display different bonding modes. The five Fe atoms lie at the vertices of a square-based pyramid; one of the basal edges is bridged by a gold atom, while the other $AuPEt_3$ group caps the square base of the Fe_5 square pyramid to give a distorted octahedral metal arrangement (**XXI**).

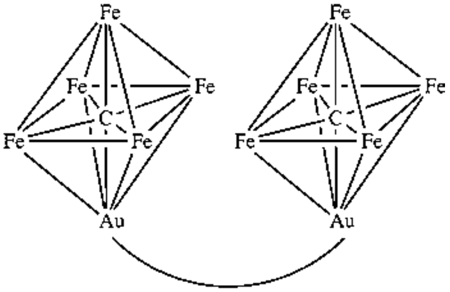


XXI

The reaction of $[NEt_4]_2[Fe_5C(CO)_{14}]$ with $(ClAu)_2(L-L)$ (L–L = dppm, dppe, dppp) depends on the stoichiometry of the process [57]. Thus, with a 1:1 molar ratio, the cluster compound $[Fe_5C(CO)_{14}\{Au_2(L-L)\}]$ was obtained. The X-ray crystal structure of the dppm compound revealed that the metal core consists of a distorted Fe_5 square-based pyramid where one gold atom caps a triangular face while the other bridges the basal edge of the same face (**XXII**). It is worth noting that this cluster is a skeletal isomer of the compound described above $[Fe_5C(CO)_{14}(AuPEt_3)_2]$. The use of a 2(iron anion):1 (gold derivative) molar ratio yielded the cluster $[NEt_4]_2[\{Fe_5C(CO)_{14}Au\}_2(L-L)]$, in which two octahedral Fe_5CAu fragments are linked by the diphosphine ligand (**XXIII**).

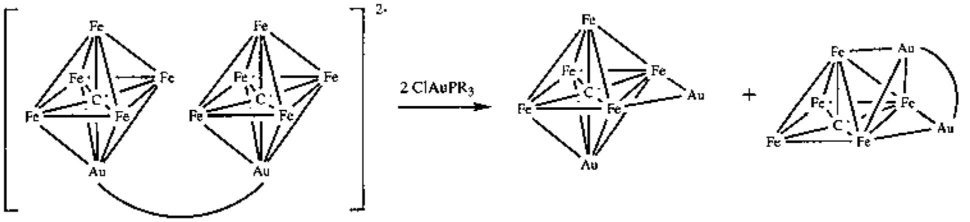


XXII



XXIII

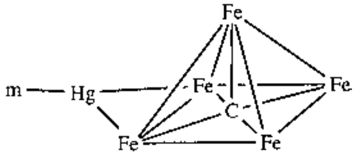
Surprisingly, the compound $[NEt_4]_2[\{Fe_5C(CO)_{14}Au\}_2(L-L)]$ reacted further with 2 equivalents of $ClAuPPh_3$ giving a mixture of two products (Chart 5):



(Chart 5)

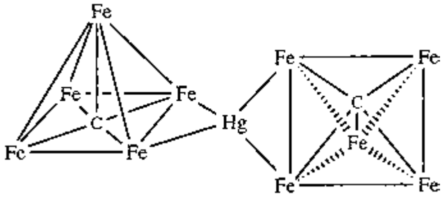
The nature of the resulting products is easily interpreted in terms of metal ligand redistribution process, which is well known in mercury chemistry but is much less usual for gold clusters [58].

On the other hand, $[Fe_5C(CO)_{15}]^{2-}$ reacts with ClHgm (m = $Mo(CO)_3Cp$, $W(CO)_3Cp$. $Fe(CO)_2Cp$, $Mn(CO)_5$, $Co(CO)_4$) to form the heptametallic clusters $[NEt_4][Fe_5C(CO)_{14}\{\mu\text{-Hgm}\}]$ [59]. The molecular structure of the anion $[Fe_5C(CO)_{14}\{\mu\text{-HgW(CO)}_3\text{Cp}\}]^-$ shows an Fe_5 square-pyramidal skeleton in which a basal edge is bridged by the $HgW(CO)_3Cp$ moiety (**XXIV**).



XXIV

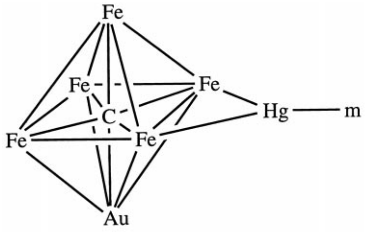
The spiro species $[Hg\{Fe_5C(CO)_{14}\}_2]^{2-}$ has been obtained by reaction of the penta-iron carbide carbon dianion with $Hg(NO_3)_2$. Its X-ray crystal structure reveals that the metal core consists of a four-coordinated mercury atom bridging the bond edges of two-square-based pyramid penta-iron units (**XXV**).



XXV

Interestingly, the ^{57}Fe Mössbauer spectra of complexes $[Fe_5C(CO)_{14}\{\mu\text{-Hg-W(CO)}_3\text{Cp}\}]^-$ and $[Fe_5C(CO)_{14}\{\mu\text{-HgFe(CO)}_2\text{Cp}\}]^-$ shows the existence of three and four types of iron site, respectively (Fig. 1).

Attempts to obtain clusters containing gold- and mercury fragments simultaneously have been successful and compounds of the type $[Fe_5C(CO)_{14}(AuPPh_3)\text{-}\{Hgm\}]$ (m = $Mo(CO)_3Cp$, $W(CO)_3Cp$) have been isolated and characterised spectroscopically, suggesting the geometry shown in **XXVI** [60].



XXVI

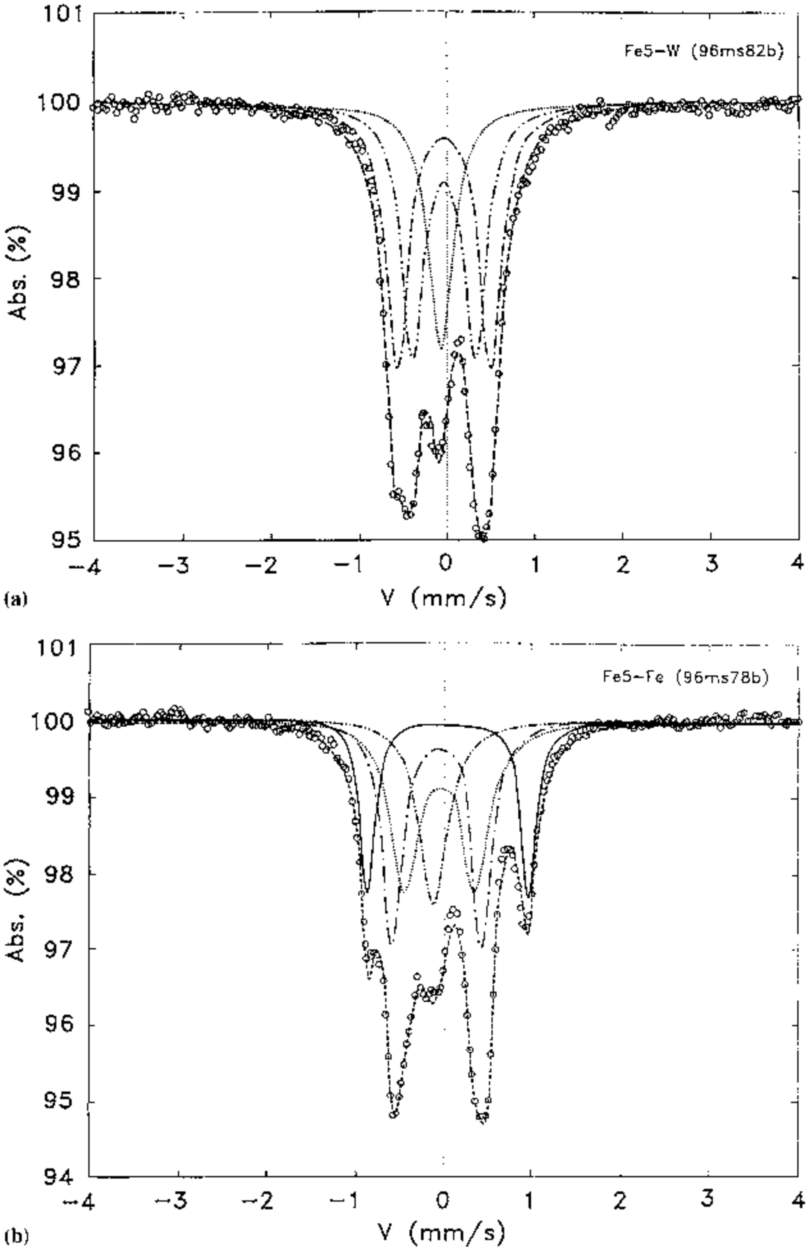
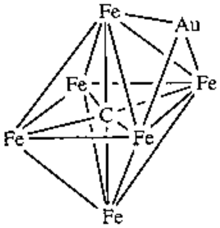


Fig. 1. (a) ^{57}Fe Mössbauer spectrum of $[NEt_4][Fe_5C(CO)_{14}\{\mu\text{-}HgW(CO)_3Cp\}]$ at 80 K: (–·–) Fe(1,4); (–··–) Fe(2,3); (· · ·) Fe(5). (b) ^{57}Fe Mössbauer spectrum of $[NEt_4][Fe_5C(CO)_{14}\{\mu\text{-}HgFe(CO)_2Cp\}]$ at 80 K: (–·–) Fe(1,4); (· · ·) Fe(2,3); (–··–) Fe(5); (—) Fe(6).

6. Hexanuclear anionic iron clusters as building blocks

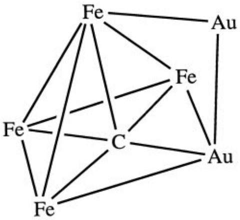
The nucleophilic character of the $[Fe_6C(CO)_{16}]^{2-}$ had been not checked until very recently. As a starting anion the carbido cluster was assumed to be a good nucleophile agent because of its two-negative charge. Additionally, the presence of the four-electron carbido ligand would favour the stabilization of the final products. With this in mind, $[Fe_6C(CO)_{16}]^{2-}$ was allowed to react with both gold and mercury complexes, affording the expected $[Fe_6C(CO)_{16}(AuPPh_3)]^-$ and $[Fe_6C(CO)_{16}\{Hgm\}]^-$ ($m = Mo(CO)_3Cp$, $W(CO)_3Cp$, $Mn(CO)_5$) anions, respectively [61]. The structure of the gold complex may be regarded as derived from that of $[Fe_6C(CO)_{16}]^{2-}$ via the capping of one triangular face of the slightly distorted octahedron by the $AuPPh_3^+$ fragment (**XXVII**). Interestingly, this is the first example reported in which a gold atom is bonded simultaneously to three iron atoms in a μ_3 bonding mode.



XXVII

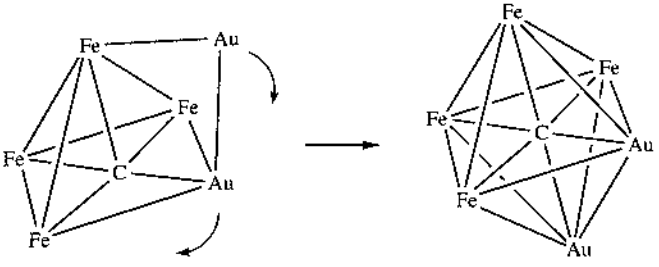
The cluster $[Hg\{Fe_6C(CO)_{16}\}_2]^{2-}$ was isolated by reaction of the iron anion with $Hg(NO_3)_2$. In an attempt to obtain the neutral compound $[Fe_6C(CO)_{15}(NO)(AuPPh_3)]$, $[Fe_6C(CO)_{16}(AuPPh_3)]^-$ was reacted with $NOBF_4$. However, the final product was found to be $[Fe_4C(CO)_{11}(NO)(AuPPh_3)]$ by X-ray diffraction. In this complex the four iron atoms are in a butterfly arrangement while the Au atom overbridges the two wingtip iron atoms [60].

Partial degradation of the starting iron cluster was observed when $[Fe_6C(CO)_{16}]^{2-}$ was allowed to react with $(ClAu)_2(dppm)$ [4]. Unexpectedly, the cluster $[Fe_4C(CO)_{12}\{Au_2(dppm)\}]$ was formed. In contrast, the use of $(ClAu)_2(dppe)$, gave the 14-metal cluster $[Et_4N]_2[\{Fe_6C(CO)_{16}Au\}_2(\mu\text{-dppe})]$, in which two Fe_6CAu fragments are linked by the bridging phosphine ligand. The molecular structure of $[Fe_4C(CO)_{12}\{Au_2(dppm)\}]$ can be described as a Fe_4 butterfly arrangement. In this, one Au atom bridges the two wingtip iron atoms while the second Au atom asymmetrically bridges the butterfly created by three iron atoms and the first gold atom (**XXVIII**).



XXVIII

Remarkably, this cluster can be considered as a skeletal isomer of $[Fe_4C(CO)_{12}(AuPEt_3)_2]$. In this, the six metal atoms define a distorted octahedron with the carbide carbon, C, lying approximately at its centre. Formally, the skeletons of $[Fe_4C(CO)_{12}(AuPEt_3)_2]$ and $[Fe_4C(CO)_{12}\{Au_2(dppm)\}]$ can interconvert to each other by moving the Au_2 fragment, (i) allowing the angle C–Fe(4)–Au(2) to bend from 87.8(4)° (dppm isomer) to about 45° (PEt_3 isomer) and (ii) creating the Au(1)–Fe(3), Au(2)–Fe(1), and Au(2)–Fe(2) bonds (Chart 6).



(Chart 6)

7. Electrochemical studies

Besides the characterization of the mixed metal clusters based mainly on spectroscopic techniques and X-ray analysis, their electrochemical properties have been investigated in some cases and a short summary is reported now.

7.1. Dinuclear iron clusters

No reports on the electrochemical behaviour of group-12 elements-iron clusters are known; however, the electrochemical study of the following iron/gold clusters $[Fe_2(CO)_7(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)]$, $[\{Fe_2(CO)_7(\mu\text{-}PPh_2)Au\}_2(diphosphine)]$ (diphosphine = dppm, dppip, dppe, dppp) and $[\{Fe_2(CO)_7(\mu\text{-}PPh_2)Au\}_3(triphos)]$ revealed an oxidation wave at about + 0.75 V and a reduction process at about − 1.4 V in all cases [17]. The reversibility of the oxidation step depends on the scan rate. Controlled potential coulometry at + 0.8 V indicated that the number of electrons transferred depends on the number of Fe_2Au units present in the compound one electron being transferred per Fe_2Au unit. During this time the violet solution changes to green and its frozen-glass EPR spectra show the resonance attributable to the radical $[Fe_2(CO)_7(\mu\text{-}PPh_2)]^{\cdot}$ by comparison with literature data [62]. The proposed mechanism is as follows:

$$[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au\}_nL] \underset{+ne^-}{\overset{-ne^-}{\rightleftharpoons}} [\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au\}_nL]^{n+}$$

$$[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au\}_nL]^{n+} \rightarrow n[Fe_2(CO)_7(\mu\text{-}PPh_2)]^{\bullet} + (Au)_nL^{n+}$$

where $L = PPh_3$, $n = 1$; L = dppm, dppip, dppe, dppp, $n = 2$; L = triphos, $n = 3$.

Similar studies for the reduction process allowed us to propose the following mechanism:

$$[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au\}_nL] \underset{-2ne^-}{\overset{+2ne^-}{\rightleftharpoons}} [\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au\}_nL]^{2n-}$$

$$[\{Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}PPh_2)Au\}_nL]^{2n-} \rightarrow n[Fe_2(CO)_7(\mu\text{-}PPh_2)]^- + (Au)_nL^{n-}$$

where $L = PPh_3$, $n = 1$; $L =$ dppm, dppip, dppe, dppp, $n = 2$; $L =$ triphos, $n = 3$.

In conclusion, it can be seen that in both the oxidation and reduction processes cleavage of Fe–Au bonds takes place. Moreover, the fact that the values of the peak potentials are nearly the same independently of the phosphine ligand indicates that the electrons involved belong to the metallic cores and that there is no electronic communication through the linking phosphine ligands.

7.2. Trinuclear iron complexes

The electrochemical behaviour of the mercury-trinuclear iron complexes $[PPh_4][Fe_3(CO)_{10}(\mu\text{-}CO)\{\mu\text{-}Hgm\}]$ has been analyzed [24]. These clusters show (i) a well-defined wave around + 0.3 V corresponding to an oxidation process; (ii) an irreversible oxidation wave at + 1.0 V; (iii) an irreversible reduction process around − 1.4 V depending on the nature of m.

Controlled potential coulometry at 0.5 V for all complexes indicated that one electron is exchanged. During that time the dark red solution changes to deep orange. The frozen-glass EPR spectra of the latter solution show a typical signal of an organometallic radical. The X-band EPR spectrum in CH_2Cl_2 is similar for all

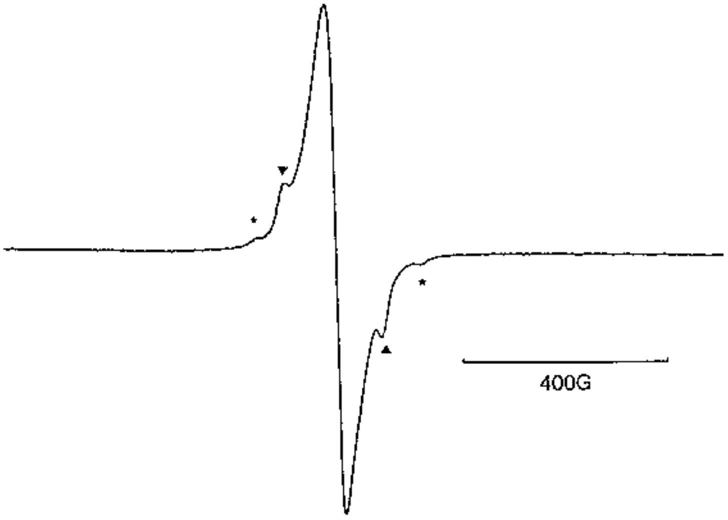


Fig. 2. X-band EPR spectrum of $[Fe_3(CO)_{11}\{HgMn(CO)_5\}]^{\bullet}$ in CH_2Cl_2 at 100 K. The signals marked with asterisks correspond to the large hyperfine coupling with the ^{201}Hg isotope ($I = 3/2$, natural abundance 13.22%).

of them (Fig. 2) and consists of a single, strong resonance centred at ca. 3267 G ($g = 2.06$) flanked by two satellite signals assigned to a hyperfine coupling with ^{199}Hg ($I = 1/2$, natural abundance 16.84%) with $a(^{199}\mathrm{Hg}) = 181$ G. Moreover, the presence of the two additional weaker signals (*) in the spectrum may indicate another hyperfine coupling with the ^{201}Hg isotope ($I = 3/2$, natural abundance 13.22%).

From these data, it appears that the unpaired electron density in the neutral radical is primarily located in the metallic core, formed by three iron and one mercury atoms. These results can be summarized according to and EC mechanism:

$$\text{(E)}\quad [\mathrm{Fe_3(CO)_{11}\{\mu\text{-}Hgm\}}]^- \underset{+1e^-}{\overset{-1e^-}{\rightleftharpoons}} [\mathrm{Fe_3(CO)_{11}\{\mu\text{-}Hgm\}}]^\bullet$$

$$\text{(C)}\quad [\mathrm{Fe_3(CO)_{11}\{\mu\text{-}Hgm\}}]^\bullet \rightarrow \mathrm{Fe_3(CO)_{12}} + \mathrm{Hgm_2} \ldots$$

The second oxidation process at + 1.0 V was observed for all the $\mathrm{Fe_3Hgm}$ complexes and was not further studied.

In the case of the reduction process, the height of the wave is double that observed for the oxidation step. This was confirmed by an exhaustive controlled potential electrolysis. It was concluded that an electrochemical step occurs,

$$[\mathrm{Fe_3(CO)_{10}(\mu\text{-}CO)\{\mu\text{-}Hgm\}}]^- + 2e^- \rightarrow [\mathrm{Fe_3(CO)_{11}\{\mu\text{-}Hgm\}}]^{3-}$$

followed by a cleavage of the trianionic species, which decompose especially in the mononuclear anionic fragments m^-, which were identified by comparison with either literature data or authenticated samples.

7.3. Higher nuclearity iron complexes

The electrochemical behaviour of the tetra-iron clusters $[\mathrm{PPN}][\mathrm{Fe_4C(CO)_{12}\{\mu\text{-}Hgm\}}]$ ($\mathrm{m} = \mathrm{Mo(CO)_3Cp}$, $\mathrm{W(CO)_3Cp}$) [5] is very similar to that described for the analogous tririon complexes. The cyclic voltammetric measurements showed three electrode processes: (i) a well-defined wave at about + 0.3 V corresponding to a quasi-reversible oxidation process of one electron, (ii) an irreversible oxidantion wave at + 1.5 V (no further studied) and (iii) an irreversible reduction process at − 1.3 V of two electrons. A typical tube EPR oxidation experiment allowed to detect the radical species $[\mathrm{Fe_4C(CO)_{12}\{\mu\text{-}Hgm\}}]^\bullet$ The X-band EPR spectrum for both complexes consists of a single strong resonance centred at ca. 3267 G ($g = 2.06$) flanked by two satellite signals assigned to a hyperfine coupling with ^{199}Hg ($a = 108$ G), indicating that the unpaired electron density in the neutral radical is mainly located in the $\mathrm{Fe_4Hg}$ core.

The electrochemical properties of clusters $[\mathrm{Fe_4C(CO)_{12}BHAu_2(AsPh_3)_2}]$ and $[\mathrm{Fe_4C(CO)_{12}BHAu_2(PPh_3)_2}]$ have been compared. Both exhibit a quasi-reversible one electron reduction at − 1.04 and − 1.10 V respectively, which is complicated by successive chemical changes, and one-electron oxidation at + 0.69 and 0.39 V. However, only the phosphine derivative can be oxidised at + 0.65 V further to the dication [50].

The electrochemical behaviour of the penta-iron clusters $[NEt_4][Fe_5C(CO)_{14}\{Hgm\}]$ was studied [59] and resulted to be somewhat different and more complicated in the cationic region than that described for the close $[PPN][Fe_4C(CO)_{12}\{\mu\text{-}Hgm\}]$ compounds. They show: (i) a one electron reduction process around -0.8 V, whose reversibility depends on the nature of m and the scan rate and (ii) a second one electron quasi-reversible reduction at -1.56 V. According to the experimental data, the mechanisms proposed for these processes are as follows:

$$[Fe_5C(CO)_{14}\{\mu\text{-}Hgm\}]^- \underset{-1e^-}{\overset{+1e^-}{\rightleftharpoons}} [Fe_5C(CO)_{14}\{\mu\text{-}Hgm\}]^{2-\bullet} \tag{i}$$

$$[Fe_5C(CO)_{14}\{\mu\text{-}Hgm\}]^{2-\bullet} \rightarrow [Fe_6C(CO)_{16}]^{2-} + m^- + Hg + \ldots$$

$$[Fe_5C(CO)_{14}\{\mu\text{-}Hgm\}]^{2-\bullet} \underset{-1e^-}{\overset{+1e^-}{\rightleftharpoons}} [Fe_5C(CO)_{14}\{\mu\text{-}Hgm\}]^{3-} \tag{ii}$$

$$[Fe_5C(CO)_{14}\{\mu\text{-}Hgm\}]^{3-} \rightarrow [Fe_5C(CO)_{14}]^{2-} + m^- + Hg$$

Finally, the electrochemical properties of the compounds $[NEt_4][Fe_6C(CO)_{16}\{Hgm\}]$ and $[NEt_4]_2[Hg\{Fe_6C(CO)_{16}\}_2]$ were not very remarkable, showing an oxidation (around $+0.9$ V) and a reduction wave (around -0.8 V), both corresponding to two electrons irreversible processes [61].

8. Concluding remarks

All the polynuclear iron anions reported show a reasonable nucleophilic character which enables them to be used as building blocks for the formation of mixed metal cluster compounds with 11- and 12-group elements. Gold- and mercury-containing clusters are more abundant than their congeners.

The nucleophilicity of the iron anion increases with its charge. In general, the incorporation of one 11- or 12-group metal fragment dramatically reduces the nucleophiliciy of the resulting cluster. Thus, the introduction of two metal fragments to an iron anion is rarely successful.

The mixed metal clusters reported are not very air-stable even in the solid state, mainly silver- and copper-containing and the iron/mercury clusters usually undergo ligand redistribution processes.

The molecular structure of the mixed metal species depends on both the nature of the starting anion and that of the incoming groups. The rigidity of dinuclear metal fragments linked by a chelated ligand may promote the formation of compounds with unexpected geometry.

Tetranuclear clusters and those containing higher nuclearities usually require the presence of a heteroatom for their stabilization. The role of the heteroelement is to provide electrons so that the cluster can get the precise electrons according to the PSEPT model. In these situation, if the heteroatom is partly exposed, it may not be innocent and react with the incoming groups to give molecules of unpredictable geometry.

The mixed transition-metal clusters show an easy electrochemical oxidation to give radical species, which have been detected by EPR spectroscopy in some cases, showing the unpaired electron density primarily located in the metallic core. The electrochemical reduction produces, in general, the easy cleavage of the Fe–M bond

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