Electrophilic additions of mono-, di- and tri-gold units to the isoelectronic [Mn₃(CO)₁₂(μ-H)]²⁻ and [Fe₃(CO)₁₁]²⁻ anions

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Abstract

The reaction of $[PPh_4]_2[Mn_3(CO)_{12}(\mu\text{-}H)]$ with $[ClAuPR_3]$ or $[(AuCl)_2(\mu\text{-}diphos)]$ in tetrahydrofuran gives the mixed manganese–gold clusters $[PPh_4][Mn_3(CO)_{12}(\mu_3\text{-}H)(\mu\text{-}AuPR_3)]$ (R = Ph (1) or Me (2)) and $[PPh_4]_2[\{Mn_3(CO)_{12}(\mu_3\text{-}H)Au\}_2(\mu\text{-}diphos)]$ (diphos = dppe (3) or dppm (4)). The reaction between the same manganese anion and $[(AuCl)_3(triphos)]$ produces $[\{Mn_3(CO)_{12}(\mu_3\text{-}H)Au\}_3(triphos)]^{3-}$ (5), $[\{Mn_3(CO)_{12}(\mu_3\text{-}H)Au\}_2(triphos)(AuCl)]^{2-}$ (6) or $[\{Mn_3(CO)_{12}(\mu_3\text{-}H)Au\}(triphos)(AuCl)_2]^-$ (7), depending on the molar ratio of the reagents. Isoelectronic iron–gold complexes $[\{Fe_3(CO)_{11}Au\}_{3-x}(triphos)(AuCl)_x]^{(3-x)-}$ (x = 0 (8), 1 (9) or 2 (10)) were obtained by the reaction of the trinuclear $[Fe_3(CO)_{11}]^{2-}$ anion with $[(AuCl)_3(triphos)]$ in the appropriate molar ratio. Attempts to obtain mixed manganese–iron–gold clusters resulted in a mixture of compounds, the nature of which has been explained in terms of metal–ligand redistribution processes.

Keywords: Gold; Manganese; Iron; Metal–metal bonds; Clusters; Electrophilic addition
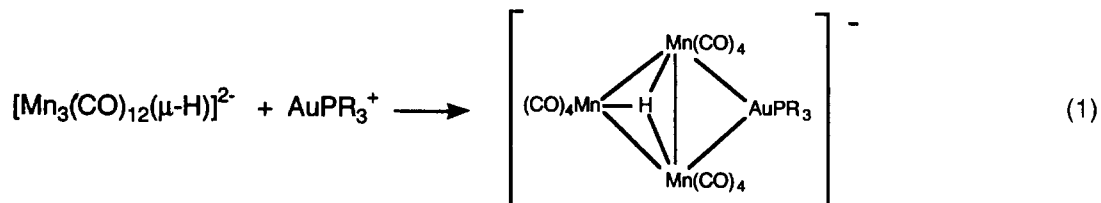
1. Introduction

The addition of mononuclear $AuPR_3^+$ fragments to carbonylmetallate anions is a well established method for the synthesis of mixed gold–transition metal clusters. However, binuclear and trinuclear gold units such as $[Au_2(diphosphine)]^{2+}$ and $[Au_3(triphosphine)]^{3+}$ have been much less explored, despite the fact that they are particularly suitable for generating higher nuclearity cluster complexes [1]. In fact, no report involving the use of trigold cationic fragments as building blocks has been published to date. Consequently, it was of interest to study the electrophilic addition of mono-, di- and tri-gold cationic fragments to $[Mn_3(CO)_{12}(\mu\text{-}H)]^{2-}$ in an attempt to determine both the stoichiometry and the structure of the resulting complexes and to compare their reactivity.

2. Results and discussion

2.1. Electrophilic addition of [AuPR₃]⁺ (R = Ph or CH₃) to [PPh₄]₂[Mn₃(CO)₁₂(μ-H)]

Addition of $[ClAuPPh_3]$ to a solution of $[PPh_4]_2$-$[Mn_3(CO)_{12}(\mu\text{-}H)]$ in THF produced good yields of the dark-green complex $(PPh_4)[Mn_3(CO)_{12}(\mu_3\text{-}H)(\mu\text{-}AuPPh_3)]$ (1) (Eq. (1)). Although attempts to obtain single crystals of this compound for an X-ray crystal structure determination were unsuccessful, the experimental data suggest that 1 contains the same metal framework as that reported for $[PPh_4][Mn_3(CO)_{12}(\mu_3\text{-}H)\{\mu\text{-}HgMo\text{-}(CO)_3Cp\}]$ [2], consisting of a planar triangulated rhombohedral metal skeleton. This assumption is also based on the isolobal relationship between HgR^+ and $AuPR_3^+$ [3]. Thus, its $\nu(CO)$ IR pattern is almost superimposable on that observed for the "$[Mn_3(CO)_{12}(\mu_3\text{-}H)]$" fragment in the corresponding mercury compounds, and appears slightly shifted to higher frequencies relative to the starting $[Mn_3(CO)_{12}(\mu\text{-}H)]^{2-}$ anion, suggesting a decrease in electron density on the manganese atoms. The ^1H NMR

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$$[Mn_3(CO)_{12}(\mu\text{-H})]^{2-} + AuPR_3^+ \longrightarrow \left[(CO)_4Mn\text{---}H \begin{array}{c} Mn(CO)_4 \\ \\ Mn(CO)_4 \end{array} AuPR_3 \right]^- \tag{1}$$
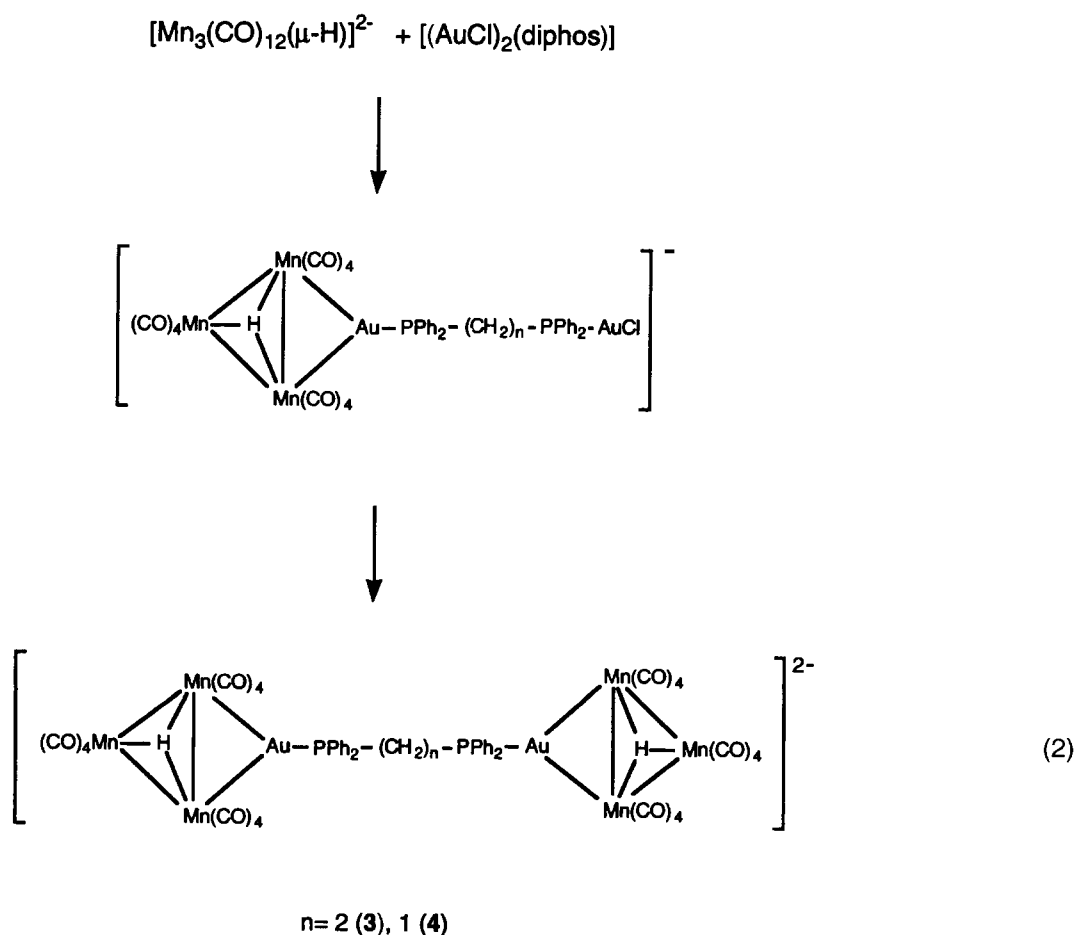
spectrum of **1** shows the presence of the hydrido-ligand at −22 ppm, indicating a bridging position [4]. The formulation of this cluster was also confirmed by the negative-ion FAB mass spectrum, which shows a parent molecular ion peak at m/z 960.7.

Neither **1** nor the complex **2**, containing the less steric congested $AuPMe_3^+$, reacted with an excess of $[ClAuPR_3]$ (R = Me, Ph) to give the pentametallic cluster $[Mn_3\text{-}(CO)_{12}(\mu_3\text{-H})(\mu\text{-AuPR}_3)_2]$ incorporating an additional $AuPR_3^+$ unit. This suggests that electronic effects should also be invoked to explain the lack of reactivity of either **1** or **2** with the gold fragments. In addition, a modification of the strategy for the synthesis of the digold adduct was carried out by adding a slight excess of HBF_4 to the medium of the reaction, given that the presence of H^+ can increase the reactivity of

the PPN^+ or Et_4N^+ salts of carbonylmetallate anions, through cation-exchange processes [5]. In our case, however, the reaction of **1** with $[ClAuPPh_3]$ in the presence of the acid gave a mixture of products from which the main complex isolated was the trihydrido compound $[Mn_3(CO)_{12}(\mu\text{-H})_3]$, as judged by its IR spectrum [6]. The formation of the last compound can be understood as the result of the protonation of $[PPh_4][Mn_3(CO)_{12}(\mu_3\text{-H})(\mu\text{-AuPPh}_3)]$, along with the substitution of H^+ by the isolobal gold unit.

2.2. Electrophilic addition of $[Au_2(diphos)_2]^{2+}$ to the manganese anion

The reaction of $[PPh_4]_2[Mn_3(CO)_{12}(\mu_3\text{-H})]$ with THF solutions of $[(AuCl)_2(\mu\text{-diphos})]$(diphos = dppe

$$[Mn_3(CO)_{12}(\mu\text{-H})]^{2-} + [(AuCl)_2(diphos)]$$

$$\downarrow$$

$$\left[(CO)_4Mn\text{---}H \begin{array}{c} Mn(CO)_4 \\ \\ Mn(CO)_4 \end{array} Au\text{---}PPh_2\text{-}(CH_2)_n\text{-}PPh_2\text{-}AuCl \right]^-$$

$$\downarrow$$

$$\left[(CO)_4Mn\text{---}H \begin{array}{c} Mn(CO)_4 \\ \\ Mn(CO)_4 \end{array} Au\text{---}PPh_2\text{-}(CH_2)_n\text{-}PPh_2\text{---}Au \begin{array}{c} Mn(CO)_4 \\ \\ Mn(CO)_4 \end{array} H\text{---}Mn(CO)_4 \right]^{2-} \tag{2}$$

n= 2 **(3)**, 1 **(4)**

$(PPh_2CH_2CH_2PPh_2)$ or dppm $(PPh_2CH_2PPh_2))$ in a 1:1 molar ratio at 238 K (Eq. 2) was monitored by ^{31}P NMR spectroscopy and the data obtained are as follows: for dppe two singlets at 64 and 23 ppm $[PPh_4^+]$ were seen along with two medium-intensity doublets centred at about 64 and 33 ppm (J(PP) = 63 Hz). The intensity of the latter peaks decreases as the reaction progresses and finally disappears. However, if the $Mn_3 : Au_2$ molar ratio is 2:1 the reaction proceeds more rapidly no doublet is then undetected.

The spectrum of the solution for dppm (molar ratio 1:1, 238 K) consists of two peaks at 61 and 23 ppm, as above, accompanied by a weak signal at 34 ppm, which is not seen when the reaction is carried out in a 2:1 molar ratio. The expected doublets were obscured by the other signals in this case. Based on these NMR data and the $\nu(CO)$ IR pattern of their solutions, we assign the peaks at 64 and 61 ppm to the anionic complexes $[\{Mn_3(CO)_{12}(\mu_3\text{-H})Au\}_2(\mu\text{-diphos})]^{2-}$ (diphos = dppe (3) or dppm (4)). Remarkably, the presence of the doublet for dppe indicates the formation of the asymmetric intermediate $[\{Mn_3(CO)_{12}(\mu_3\text{-H})Au\}(\mu\text{-dppe})-(AuCl)]^-$, which would result from the direct replacement of only one chloride from the starting digold derivative by the $[Mn_3(CO)_{12}(\mu\text{-H})]$ unit. It is worth emphasizing that this is the first time the intermediate

involved in such a process has been detected spectroscopically. Compound 4 probably follows the same two-step chloride substitution pathway, although no spectroscopic evidence of the formation of $[\{Mn_3-(CO)_{12}(\mu_3\text{-H})Au\}(\mu\text{-dppm})(AuCl)]^-$ is available.

The weak peak at 34 ppm present in the solutions containing 4 may correspond to an unidentified symmetric derivative but considering the tendency of the moiety $[Au_2(dppm)]^{2+}$ to bind μ_2 to a preformed cluster [1c], some pentanuclear $[Mn_3(CO)_{12}(\mu_3\text{-H})Au_2-(dppm)]$ may be formed during the process. Unfortunately, the instability of this cluster precluded its isolation and characterization.

Work-up of THF solutions containing 3 and 4 gave good yields of dark-green complexes which were characterized analytically and spectroscopically. Although the molecular ion was not observed in the negative-ion FAB mass spectrum, the peaks of $[Mn_3(CO)_{12}(\mu_3\text{-H})Au]^-$ and its progressive loss of carbonyl groups, from 2 to 11, confirm the presence of this moiety, which was also seen in the FAB mass spectrum of 1.

The behaviour exhibited by the manganese anion in reacting with $[Au_2(diphos)]^{2+}$ to give complexes with two Mn_3Au fragments linked by the diphosphine, rather than the neutral species $[[Mn_3(CO)_{12}(\mu_3\text{-H})Au_2(diphos)]$, can be understood by examining the

$$[Mn_3(CO)_{12}(\mu\text{-H})]^{2-} + (AuCl)_3(triphos) \longrightarrow$$

(7)

(6)

(5)

(3)

$\nabla Mn \nabla = [Mn_3(CO)_{12}(\mu_n\text{-H})]$

$= CH_3C(CH_2PPh_2)_3$
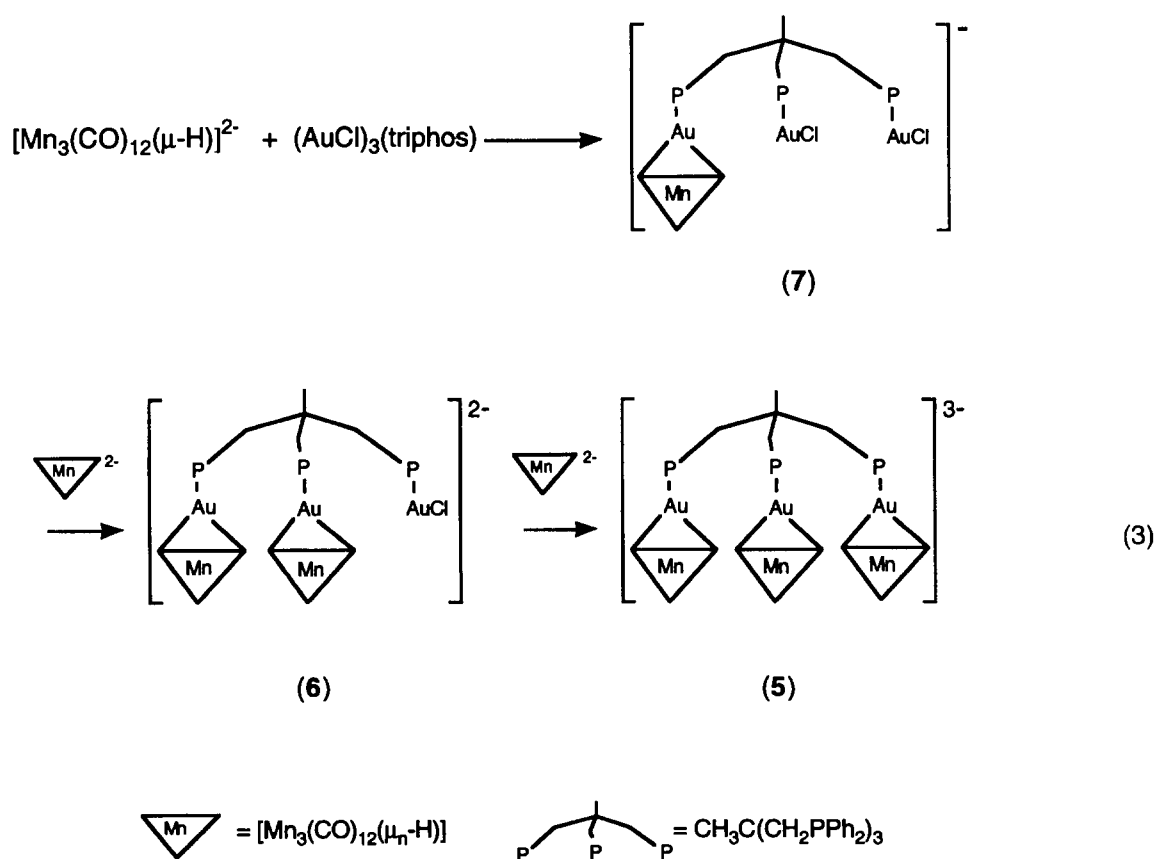
topology of the highest occupied molecular orbitals of $[Mn_3(CO)_{12}(\mu\text{-H})]^{2-}$. This must be responsible for the donation of electron density from the manganese anion to the $AuPR_3$ fragment. Although the general aspects of the electronic structure and bonding of $[Mn_3(CO)_{12}(\mu\text{-H})]^{2-}$ have been discussed in detail in a previous paper [2] and will not be analysed here, we can summarize the results by emphasizing that the manganese anion is particularly appropriate for generating metal clusters in which a gold fragment bridges an Mn–Mn edge of the triangular Mn_3 starting cluster.

2.3. Electrophilic addition of $[Au_3(triphos)]^{3+}$ to $[Mn_3(CO)_{12}(\mu\text{-H})]^{2-}$

Despite the fact that the trigold derivative $[(AuCl)_3(triphos)]$ [7] (triphos = $CH_3C(CH_2PPh_2)_3$) has been known for several years, no report describing its electrophilicity towards carbonylmetallate anions has been published. Interest in this species arises from its ability to form a wide range of mixed transition metal–gold clusters. Our first aim was to obtain Mn–Au clusters with the Mn_3Au framework displayed in complexes **1–4** by making the trigold derivative react with 1, 2 or 3 equiv. of $[PPh_4]_2[Mn_3(CO)_{12}(\mu\text{-H})]$ (Eq. (3)). The processes were carried out in THF at 258 K and in all cases dark-green crystals were obtained in moderate to good yields. Although the $\nu(CO)$ IR pattern is the same for the three products, $[PPh_4]_3[\{Mn_3(CO)_{12}(\mu_3\text{-}H)Au\}_3$ (triphos)] **(5)**, $[PPh_4]_2[\{Mn_3(CO)_{12}(\mu_3\text{-}$

$H)Au\}_2(triphos)(AuCl)]$ **(6)** and $[PPh_4][\{Mn_3(CO)_{12}(\mu_3\text{-}H)Au\}(triphos)(AuCl)_2]$ **(7)**, as expected, their $\delta^{31}P$ spectra show unambiguous distinctions between them (see Experimental section). The hydrido ligand is also revealed by ^1H NMR spectroscopy. We were not able to obtain single crystals for an X-ray crystal structure determination, but microanalyses and IR, NMR and FAB mass spectrometry strongly support the formulations. The negative-ion FAB mass spectrum of **5–7** are nearly identical with that of **3**. Although the molecular ion is not observed, the most intense set of peaks confirms the presence of the $[Mn_3(CO)_{12}(\mu_3\text{-}H)Au]^-$ fragment in all of them. The fact that there are peaks of greater m/z than this and that the dppe and triphos compounds exhibit similar phenomena suggest that further species are formed by ion–molecule reactions in the spectrometer [8].

We examined the reactivity of **5** with the iron anion $[Fe_3(CO)_{11}]^{2-}$ to determine whether the nucleophilicity of the latter anion in presence of mercury [9] or gold fragments [1c] could promote the replacement of the manganese units attached to the gold atoms. However, **5** did not react with $[Fe_3(CO)_{11}]^{2-}$ even at room temperature, as judged to ^{31}P NMR spectroscopy, and **5** was recovered unaltered. In addition, we studied the reaction between **5** and **7** in an attempt to observe metal–ligand redistribution processes. The ^{31}P NMR spectra of the THF solution at the mixture showed that an equilibrium was reached (Eq. (4)) between the species **5**, **6** and **7**. From the peak-area ratio it was deduced that the equi-

(5)

$+$

(7)

(6)

$$\text{(4)}$$

(6)   + [Fe₃(CO)₁₁]²⁻   →   (5)

(5)   **(8)**

  = [Fe₃(CO)₁₁]
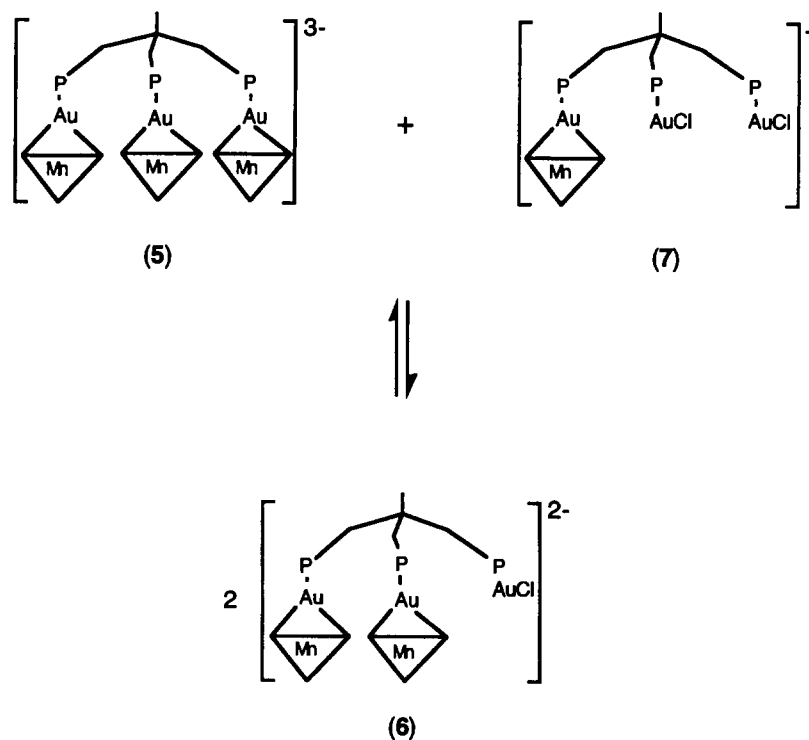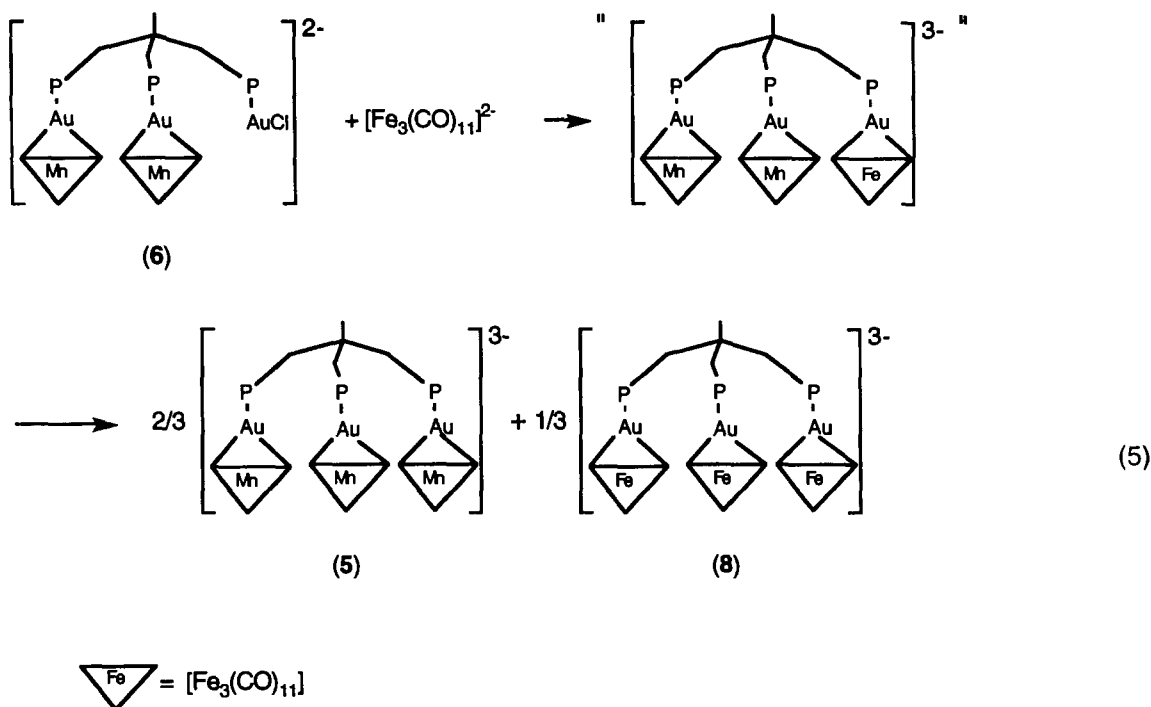
librium position of Eq. (4) is shifted towards the left-hand side.

Having determined the inertness of **5** to metal–ligand exchange processes, we assumed that **6** might be an intermediate in the formation of mixed Mn–Fe–Au clusters by direct substitution of the Cl atom (of the AuCl unit) for the $[Fe_3(CO)_{11}]^{2-}$ anion. This reaction in THF at 258 K unexpectedly gave a mixture of **5** and the new compound $[\{Fe_3(CO)_{11}Au\}_3(triphos)]^{3-}$ (**8**), which would result from the disproportionation of $[\{Mn_3-(CO)_{12}(\mu_3\text{-H})Au\}_2\{Fe_3(CO)_{11}Au\}(triphos)]^{3-}$ (Eq. (5)).

2.4. Electrophilic addition of $[Au_3(triphos)]^{3+}$ to $[Fe_3(CO)_{11}]^{2-}$

The tendency of metal clusters to give the most symmetric species is well known in the chemistry of mercury, but there are fewer examples involving ligand-redistribution processes in gold chemistry [10]. To gain insight into the generality of the process, we

attempted the syntheses of the analogous iron–gold complexes $[PPh_4]_3[\{Fe_3(CO)_{11}Au\}_3(triphos)]$ (**8**), $[PPh_4]_2[\{Fe_3(CO)_{11}Au\}_2(triphos)(AuCl)]$ (**9**) and $[PPh_4][\{Fe_3(CO)_{11}Au\}(triphos)(AuCl)_2]$ (**10**) by the reaction of $[(AuCl)_3(triphos)]$ with $[PPh_4]_2[Fe_3(CO)_{11}]$ in the appropriate molar ratios (Scheme 1). Complexes **8**, **9** and **10** were characterized in the usual manner (see Experimental section). The cluster units are isostructural with $[Fe_3(CO)_{11}\{\mu\text{-AuPPh}_3\}]^-$ [1c]. As with compounds **5–7** the parent molecular ion is not detected in the negative-ion FAB mass spectra of these compounds, but the most intense peaks correspond to the $[Fe_3(CO)_{11}Au]^-$ fragment and the stripping of 1–11 carbonyl groups. Hence the formation of this metal cluster unit was confirmed.

We found that **8** was also inert towards $[Mn_3(CO)_{12}(\mu\text{-H})]^{2-}$ but it reacted with **10** to give a mixture of **8**, **9** and **10**, in an equilibrium slightly shifted to the left (^{31}P NMR spectroscopy). The attack of 1 equiv. of $[Mn_3(CO)_{12}(\mu\text{-H})]^{2-}$ on **9** resulted in the symmetric species **5** and **8** in a molar ratio of about 1:2, the

(8)   **(9)**   **(10)**
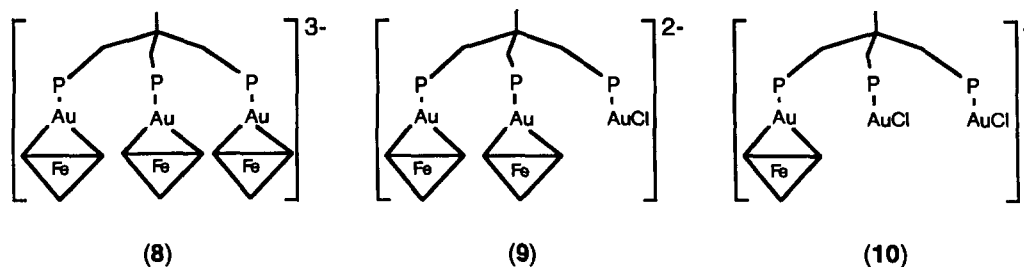
Scheme 1.

pattern also observed for the reaction between [Fe$_3$(CO)$_{11}$]$^{2-}$ and **6** (Eq. (5)). Therefore, we suggest that the final products are the result of a process involving metal–ligand redistribution from [{Fe$_3$(CO)$_{11}$Au}$_2$-{Mn$_3$(CO)$_{12}$(μ_3-H)Au}(triphos)]$^{3-}$. Finally, the major product obtained by allowing **10** to react with [Mn$_3$(CO)$_{12}$(μ-H)]$^{2-}$ or **7** to react with [Fe$_3$(CO)$_{11}$]$^{2-}$ is complex [{Fe$_3$(CO)$_{11}$Au}{Mn$_3$(CO)$_{12}$(μ_3-H)Au}(triphos)(AuCl)]$^{2-}$ (**11**), which, although not isolated, is detected in THF solution along with some **9** and **6** by ^{31}P NMR spectroscopy with resonances at $\delta = 55.2$ (*P*AuMn$_3$), 38.5 (*P*AuFe$_3$) and 18.9 (*P*AuCl) ppm (Eq. (6)). The latter compounds may be formed by the symmetrization of **11**.

Our results shed light on the role of the AuCl group attached to triphos. The presence of AuCl groups in the clusters seems to inhibit the metal ligand redistribution processes, sometimes to a considerable extent. For example, Eqs. (4) and (6) are equilibrium reactions in which the species **7** and **11**, respectively, are the major products. However, compounds [{Fe$_3$(CO)$_{11}$Au}$_2$-{Mn$_3$(CO)$_{12}$(μ_3-H)Au}(triphos)]$^{3-}$ and [{Fe$_3$(CO)$_{11}$-Au}{Mn$_3$(CO)$_{12}$(μ_3-H)Au}$_2$(triphos)]$^{3-}$ redistribute completely, giving mixtures of the most symmetric compounds, **5** and **8** (Eq. (5)). The difference in the behaviour of the AuCl and AuM$_3$ fragments also has a precedent in the chemistry of mercury. For instance, [Cp(CO)$_3$MoHgCl] is inert towards disproportionation, whereas the related [Cp(CO)$_3$MoHg{Fe$_2$(CO)$_7$(μ-PPh$_2$)}] spontaneously redistributes to [Hg{Fe$_2$(CO)$_7$(μ-PPh$_2$)}$_2$] [11]. The nature of the bonding in the AuCl or HgCl groups, that is, two-centre, two-electron, as compared with the corresponding AuM$_3$ or HgM$_2$ fragments, three-centre, two-electron, may be responsible for the difference in the behaviour of these two types of metal fragment.

3. Experimental section

3.1. Synthesis of [PPh$_4$][Mn$_3$(CO)$_{12}$(μ_3-H)AuPR$_3$] (R = Ph (1) or Me (2))

Solid [AuClPPh$_3$] (0.29 g, 0.59 mmol) was added to a suspension of [PPh$_4$]$_2$[Mn$_3$(CO)$_{12}$(μ-H)] (0.70g, 0.59 mmol) in THF (40 ml) at 258 K. The mixture turned

(11)

(6)

(9)
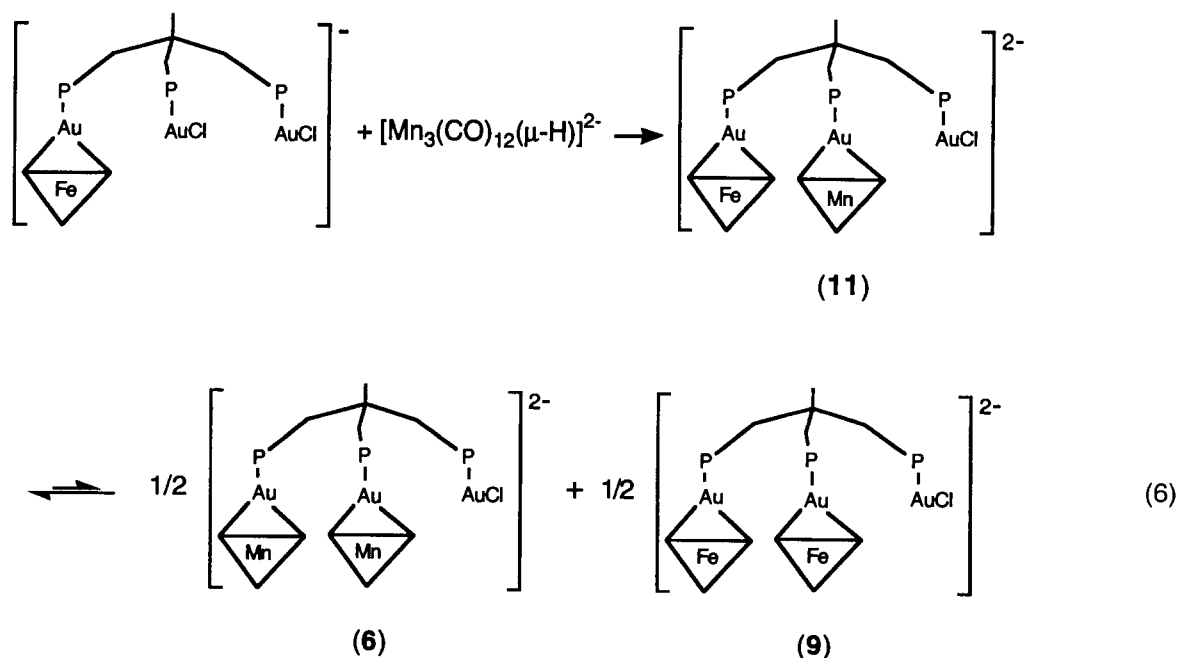
green immediately and was stirred for 5 h and then filtered through Celite. After removing the THF under vacuum, the residue was dissolved in cold acetone and concentrated, and methanol was added. Upon cooling, dark-green microcrystals were deposited, which were collected by filtration. Yield: 0.45 g, 59%. IR (THF, cm^{-1}), ν(CO) stretch 2049(w), 1991(m), 1981(m), 1966(s), 1942(w), 1925(m), 1885(w); ^{31}P{^{1}H} NMR (240 K, THF, δ (ppm)) 63.9 (*P*Au), 23.3 (*P*Ph$_4^+$); ^{1}H NMR (240 K, acetone-d_6, δ (ppm)) −22 (Mn$_3$H). Anal. Calc. for C$_{54}$H$_{36}$AuMn$_3$O$_{12}$P$_2$: C, 49.9; H, 2.77. Found: C, 50.0; H, 2.73% FABS (−): m/z Calc.: 960.75; found: 960.70.

This synthesis also applies to (PPh$_4$)[Mn$_3$(CO)$_{12}$(μ_3-H)AuPMe$_3$] (**2**). IR (THF, cm^{-1}), ν(CO) stretch 2050(w), 1995(w), 1980(m), 1970(s), 1955(s), 1935(sh), 1918(m), 1870(w); ^{31}P{^{1}H} NMR (240 K, THF, δ (ppm)) 20.3 (*P*Au), 23.2 (*P*Ph$_4^+$). Anal. Calc. for C$_{39}$H$_{30}$AuMn$_3$O$_{12}$P$_2$: C, 42.0; H, 2.69. Found: C, 41.6; H, 2.64%.

3.2. Synthesis of [PPh$_4$]$_2$[{Mn$_3$(CO)$_{12}$(μ_3-H)Au}$_2$(diphos)] (3 and 4)

Solid [(AuCl)$_2$dppm] (0.20 g, 0.24 mmol) was added to a suspension of [PPh$_4$]$_2$[Mn$_3$(CO)$_{12}$(μ-H)] (0.55 g, 0.47 mmol) in THF (25 ml) at 258 K. The mixture turned green immediately and was stirred for 1–2 h and then filtered through Celite. After removing the THF under vacuum, cold methanol was added and the solution was filtered immediately. A green solid that decomposed in few days under N$_2$ was obtained. Yield: 0.40 g, 70%. IR (THF, cm^{-1}), ν(CO) stretch 2051(w), 1992(m), 1983(m), 1967(s), 1943(w), 1928(m), 1880(w); ^{31}P{^{1}H} NMR (240 K, THF, δ (ppm)) 60.7 (*P*AuMn$_3$), 22.7 (*P*Ph$_4^+$). Anal. Calc.: C, 47.3; H, 2.60. Found: C, 46.7; H, 2.73%.

This method was also applied to [PPh$_4$]$_2$[{Mn$_3$(CO)$_{12}$(μ_3-H)Au}$_2$dppe] (**3**). IR (THF, cm^{-1}), ν(CO) stretch 2051(w), 1990(m), 1983(m), 1965(s), 1994(w), 1928(m), 1885(w); ^{31}P{^{1}H} NMR (240 K, THF, δ (ppm)) 63.6 (*P*Au), 22.8 (*P*Ph$_4^+$); ^{1}H NMR (240 K, acetone-d_6, δ (ppm)) −17 (Mn$_3$H, br.). Anal. Calc. for C$_{98}$H$_{66}$Au$_2$Mn$_6$O$_{24}$P$_4$: C, 47.5; H, 2.67. Found: C, 47.5; H, 2.69%.

3.3. Synthesis of [PPh$_4$]$_3$[{Mn$_3$(CO)$_{12}$(μ_3-H)Au}$_3$(triphos)] (5)

Solid [(AuCl)$_3$(triphos)] (0.32 g, 0.24 mmol) was added to a suspension of [PPh$_4$]$_2$[Mn$_3$(CO)$_{12}$(μ-H)] (0.87 g, 0.74 mmol) in THF (35 ml) at 258 K. The mixture turned green immediately and was stirred for 6 h; then more [PPh$_4$]$_2$[Mn$_3$(CO)$_{12}$(μ-H)] (0.29 g, 0.24 mmol) was added and the solution was stirred overnight. The mixture was filtered and the solvent was evaporated

from the filtrate. A dark-green solid was obtained by adding methanol and filtering immediately. Yield: 0.59 g, 65%. IR (THF, cm^{-1}), ν(CO) stretch 2050(w), 1992(sh), 1983(m), 1966(s), 1942(w), 1926(m), 1880(w); ^{31}P{^{1}H} NMR (240 K, THF, δ (ppm)) 56.5 (*P*AuMn$_3$), 23.1, (*P*Ph$_4^+$). ^{1}H NMR (240 K, acetone-d_6, δ (ppm)) −17 (Mn$_3$H, br.). Anal. Calc. for C$_{149}$H$_{102}$Au$_3$Mn$_9$O$_{36}$P$_6$: C, 47.8; H, 2.73. Found: C, 47.5; H, 2.77%.

3.4. Synthesis of [PPh$_4$]$_2$[{Mn$_3$(CO)$_{12}$(μ_3-H)Au}$_2$(triphos)(AuCl)] (6)

Solid [(AuCl)$_3$(triphos)] (0.34 g, 0.26 mmol) was added to a suspension of [PPh$_4$]$_2$[Mn$_3$(CO)$_{12}$(μ-H)] (0.70 g, 0.59 mmol) in THF (50 ml) at 258 K. The green solution was stirred for 4 h, then filtered, and the filtrate was reduced to 5–10 ml. Hexane (4 ml) was added and the resulting solution was left in a freezer overnight. The dark-green crystals obtained were collected by filtration and dried in vacuo. Yield: 0.42 g, 55%. IR (THF, cm^{-1}), ν(CO) stretch 2051(w), 1993(m), 1982(m), 1967(s), 1941(w), 1927(m), 1881(w); ^{31}P{^{1}H} NMR (240 K, THF, δ (ppm)) 53.9 (*P*AuMn$_3$), 19.1 (*P*AuCl), 23.2 (*P*Ph$_4^+$). ^{1}H NMR (240 K, acetone-d_6, δ (ppm)) −17 (Mn$_3$H, br.). Anal. Calc. for C$_{113}$H$_{81}$Au$_3$ClMn$_6$O$_{24}$P$_5$: C, 46.2; H, 2.76. Found: C, 46.9; H, 2.70%.

3.5. Synthesis of [PPh$_4$][{Mn$_3$(CO)$_{12}$(μ_3-H)Au}(triphos)(AuCl)$_2$] (7)

Solid [(AuCl)$_3$(triphos)] (0.31 g, 0.23 mmol) was added to a suspension of [PPh$_4$]$_2$[Mn$_3$(CO)$_{12}$(μ-H)] (0.25 g, 0.21 mmol) in THF (40 ml) at 258 K. The mixture turned green immediately and was stirred for 2 h. The solution was filtered and the solvent was evaporated from the filtrate. Cold methanol was added and the resulting solution was filtered immediately. Yield: 0.27 g, 60%. IR (THF, cm^{-1}), ν(CO) stretch 2051(w), 1992(m), 1984(m), 1968(s), 1945(w), 1928(m), 1880(w); ^{31}P{^{1}H} NMR (240 K, THF, δ (ppm)) 51.7 (*P*AuMn$_3$), 17.1 (*P*AuCl), 23.2 (*P*Ph$_4^+$). ^{1}H NMR (240 K, acetone-d_6, δ (ppm)) −17 (Mn$_3$H, br.). Anal. Calc. for C$_{77}$H$_{60}$Au$_3$Cl$_2$Mn$_3$O$_{12}$P$_4$: C, 43.4; H, 2.82. Found: C, 43.9; H, 2.90%.

3.6. Synthesis of [PPh$_4$]$_3$[{Fe$_3$(CO)$_{11}$Au}$_3$(triphos)] (8)

Solid [(AuCl)$_3$(triphos)] (0.34 g, 0.26 mmol) was added to a suspension of [PPh$_4$]$_2$[Fe$_3$(CO)$_{11}$] (1.20 g, 1.04 mmol) in THF (40 ml) at 258 K. The mixture was stirred for 7–8 h, then filtered through Celite and the filtrate was evaporated to 15–20 ml and hexane was then added. A dark-violet solid was obtained overnight. Yield: 0.51 g, 54%. IR (KBr, cm^{-1}), ν(CO) stretch

2038(m), 1965(s), 1934(m), 1910(m), 1715(w); $^{31}P\{^1H\}$ NMR (240 K, THF, δ (ppm)) 41.3 ($PAuFe_3$), 23.2 (PPh_4^+). Anal. Calc. for $C_{146}H_{99}Au_3Fe_9O_{33}P_6$: C, 47.9; H, 2.71. Found: C, 47.6; H, 2.75%.

3.7. Synthesis of [PPh$_4$]$_2$[{Fe$_3$(CO)$_{11}$Au}$_2$(triphos)-(AuCl)] (9)

To a suspension of $[PPh_4]_2[Fe_3(CO)_{11}]$ (0.42 g, 0.36 mmol) in 30 ml of THF at 258 K solid $[(AuCl)_3(triphos)]$ (0.20 g, 0.15 mmol) was added. After 4 h of stirring the compound $[\{Fe_3(CO)_{11}Au\}_2(triphos)(AuCl)]^{2-}$ was formed as shown by NMR spectroscopy, but weak signals from compounds 8 and 10 were also seen. Spectroscopic data for $[\{Fe_3(CO)_{11}Au\}_2(triphos)-(AuCl)]^{2-}$: IR (THF, cm^{-1}), ν(CO) stretch 2038(m), 1966(s), 1935(sh), 1915(sh), 1716(w); $^{31}P\{^1H\}$ NMR (240 K, THF, δ (ppm)) 40.0 ($PAuFe_3$), 17.8 ($PAuCl$).

3.8. Synthesis of [PPh$_4$][{Fe$_3$(CO)$_{11}$Au}(triphos)-(AuCl)$_2$] (10)

Solid $[(AuCl)_3(triphos)]$ (0.22 g, 0.17 mmol) was added to a suspension of $[PPh_4]_2[Fe_3(CO)_{11}]$ (0.19 g, 0.16 mmol) in THF (25 ml) at 258 K. The mixture was stirred for 7 h, then filtered and the solvent was partially removed from the filtrate. After hexane addition a dark-violet precipitate was obtained, which was filtered off and dried in vacuo. Yield: 0.34 g, 50%. IR (KBr, cm^{-1}), ν(CO) stretch 2040(m), 1966(s), 1935(sh), 1915(sh), 1716(w); $^{31}P\{^1H\}$ NMR (240 K, THF, δ (ppm)) 37.1 ($PAuFe_3$), 17.6 ($PAuCl$), 23.2 (PPh_4^+). Anal. Calc. for $C_{76}H_{59}Au_3Cl_2Fe_3O_{11}P_4$: C, 43.4; H, 2.81. Found: C, 42.8; H, 2.87%.

3.9. Reaction of [PPh$_4$][{Fe$_3$(CO)$_{11}$Au}(triphos)-(AuCl)$_2$] (10) with [PPh$_4$]$_2$[Mn$_3$(CO)$_{12}$(μ-H)]

A solution of 10 was prepared by treating $[PPh_4]_2[Fe_3(CO)_{11}]$ (0.19 g, 0.16 mmol) with solid $[(AuCl)_3(triphos)]$ (0.22 g, 0.17 mmol) in THF (25 ml) at 258 K, as described above. After stirring for 7 h, $[PPh_4]_2[Mn_3(CO)_{12}(\mu-H)]$ (0.20 g, 0.17 mmol) was added. The new compound $[\{Fe_3(CO)_{11}Au\}\{Mn_3(CO)_{12}-(\mu_3-H)Au\}(triphos)(AuCl)]^{2-}$ (11), showing $^{31}P\{^1H\}$ NMR signals at 55.2 ($PAuMn_3$), 38.5 ($PAuFe_3$) and 18.9 ($PAuCl$) was observed. However, weak signals of the complexes $[PPh_4]_2[\{Mn_3(CO)_{12}(\mu_3-H)Au\}_2(triphos)(AuCl)]$ (6), $[PPh_4]_2[\{Fe_3(CO)_{11}Au\}_2(triphos)-(AuCl)]$ (9), $[PPh_4][\{Mn_3(CO)_{12}(\mu_3-H)Au\}(triphos)-(AuCl)_2]$ (7) and $[PPh_4][\{Fe_3(CO)_{11}Au\}(triphos)-(AuCl)_2]$ (10) were also present. A solid was obtained by working up as for 10, but all attempts at recrystallization increased the intensity of the signals of the other compounds in the $^{31}P\{^1H\}$ NMR spectrum.

This procedure was also applied to the reaction be-

tween 7 and $[PPh_4]_2[Fe_3(CO)_{11}]$ and similar results were obtained.

3.10. Reaction of [PPh$_4$]$_2$[{Mn$_3$(CO)$_{12}$(μ$_3$-H)Au}$_2$(triphos) (AuCl)] (6) with [PPh$_4$]$_2$[Fe$_3$(CO)$_{11}$]

A solution of 6 was obtained by stirring 0.70 g of $[PPh_4]_2[Mn_3(CO)_{12}(\mu-H)]$ and 0.35 g of $[(AuCl)_3(triphos)]$ in 50 ml of THF at 258 K for 4h. Then $[PPh_4]_2[Fe_3(CO)_{11}]$ (0.31 g, 0.27 mmol) was added. After 2 h a large quantity of $[PPh_4]_2[\{Mn_3(CO)_{12}(\mu_3-H)Au\}_2(triphos)(AuCl)]$ (6) remained, but other signals in the $^{31}P\{^1H\}$ NMR spectrum indicated the presence of $[PPh_4]_3[\{Mn_3(CO)_{12}(\mu_3-H)Au\}_3(triphos)]$ (5) ($\delta = 56.5$) and $[PPh_4]_3[\{Fe_3(CO)_{11}Au\}_3(triphos)]$ (8) ($\delta = 41.3$), which were the only ultimate products.

3.11. Reaction of [PPh$_4$]$_3$[{Mn$_3$(CO)$_{12}$(μ$_3$-H)Au}$_3$(triphos)] (5) with [PPh$_4$][{Mn$_3$(CO)$_{12}$(μ$_3$-H)Au}(triphos)(AuCl)$_2$] (7)

A solution of $[PPh_4]\{Mn_3(CO)_{12}(\mu_3-H)Au\}(triphos)(AuCl)_2]$ (0.05 g, 0.02 mmol) in 5 ml of THF was added to a solution of $[PPh_4]_3[\{Mn_3(CO)_{12}(\mu_3-H)Au\}_3(triphos)]$ (0.09 g, 0.02 mmol) in 5 ml of THF at 258 K. After stirring for 3 h, signals of $[PPh_4]_3[\{Mn_3-(CO)_{12}(\mu_3-H)Au\}_3(triphos)]$ (5), $[PPh_4]_2[\{Mn_3(CO)_{12}-(\mu_3-H)Au\}_2(triphos)(AuCl)]$ (6) and $[PPh_4][\{Mn_3-(CO)_{12}(\mu_3-H)Au\}(triphos)(AuCl)_2]$ (7) were seen in the $^{31}P\{^1H\}$ NMR spectrum. The spectrum had not changed 20 h later.

However, when solutions of $[PPh_4]_3[\{Fe_3(CO)_{11}-Au\}_3(triphos)]$ (8) and $[PPh_4]$ $[\{Fe_3(CO)_{11}Au\}(triphos)(AuCl)_2]$ (10) were mixed, signals of the three compounds $[PPh_4]_3[\{Fe_3(CO)_{11}Au\}_3(triphos)]$ (8) ($\delta = 41.3$), $[PPh_4]_2[\{Fe_3(CO)_{11}Au\}_2(triphos)(AuCl)]$ (9) ($\delta = 40.0$ and 17.8) and $[PPh_4][\{Fe_3(CO)_{11}Au\}(triphos) (AuCl)_2]$ (10) ($\delta = 37.1$ and 17.6) were observed in the $^{31}P\{^1H\}$ NMR spectrum, indicating an equilibrium similar to that observed for 5, 6 and 7.

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