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Anionic and neutral spiked triangle clusters of mercury: a comparative study of the metal ligand redistribution process

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Abstract

The action of the NEt_4^+ salts of the anions $[Fe_2(CO)_8]^{2-}$ and $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ on ClHg–m complexes (m = $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Mn(CO)_5$, $Co(CO)_4$, and $Fe(CO)_2Cp$) has been investigated. In the first case, anionic spiked triangle clusters of formula $[Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}Hg\text{–}m)]^-$ were obtained in high yields, and no metal ligand redistribution reactions were detected. However, the action of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ on the same bimetallic transition metal-mercury compounds gave the neutral species $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}Hg\text{–}m)]$, which spontaneously redistributed to $[Hg\{Fe_2(CO)_7(\mu\text{-}PPh_2)\}_2]$ and m_2Hg. Only the molybdenum derivative could be isolated in pure form. The different behaviour of the two series of complexes in the redistribution process is discussed.

Although the redistribution chemistry of organomercurial compounds has been extensively investigated, analogous reactivity for heterometallic complexes of mercury is less well documented [1]. In general, it is observed that most of the two-center two-electron bonded transition-metal mercury compounds redistribute to unsymmetric species [2], e.g.:

$$[Hg\{Pt(C_6Cl_5)(PPh_3)_2\}_2] + Hg\{Fe(CO)_2Cp\}_2 \rightarrow 2[Cp(OC)_2FeHgPt(C_6Cl_5)(PPh_3)_2] \quad (1)$$

In contrast, with complexes containing a three-center two-electron mercury-transition metal bond formation of the symmetric species is favored [3], e.g.:

$$2[Ru_3(\mu\text{-}HgX)(CO)_9(\mu_3\text{-}C_2\text{-t-Bu})] \rightarrow [Ru_3(CO)_9(\mu_3\text{-}C_2\text{-t-Bu})]_2Hg + HgX_2 \quad (2)$$

These observations can be readily accounted for in terms of kinetic factors if it is assumed that the preferred pathway for the redistribution reactions involves a bimolecular, associative process. This process, believed to proceed through a four-

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center bridged transition state [4], would involve an increase in the coordination number of the mercury atom, which is not unreasonable for complexes containing two- or three-coordinate mercury atoms. However such a process is unlikely for the mercury in the ***Spiro-type*** compound in Eq. 2 because it is already four-coordinate, and coordination numbers greater than four are not normally observed for mercury in transition metal complexes.

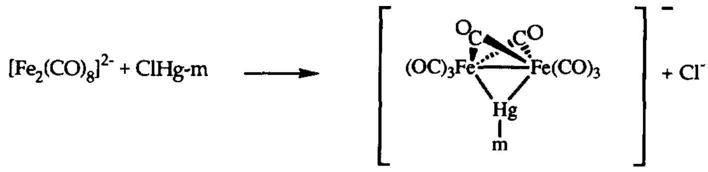
The assumption that redistribution reactions occur via an associative mechanism prompted us to attempt the synthesis of the anionic spiked triangle clusters with a three-center two-electron-transition metal bond of formula $[Fe_2(CO)_8(\mu\text{-Hg–m})]^-$, where m is a metal fragment. It was assumed that the negative charge on these derivatives would preclude unwanted symmetrization processes and facilitate the isolation of their salts. In fact, to our knowledge, the only mercury complex with such a geometry so far described is $[Mn_2(\mu\text{-HgCl})(\mu\text{-PPh}_2)(CO)_8]$[3b], which tends to disproportionate readily to $[Hg\{Mn_2(\mu\text{-PPh}_2)(CO)_8\}_2]$ and $HgCl_2$.

The synthesis of such derivatives was accomplished by using redox condensation reactions between anionic and cationic metal complexes, a well known route to such mixed-metal clusters. In addition, we describe below the synthesis and the ligand redistribution of the structurally close neutral tetrametallic derivatives of the type $[Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-PPh}_2)(\mu\text{-Hg–m})]$, in order to make comparisons between the behaviour of the two series of compounds in metal ligand redistribution reactions.

Results and discussion

(a) Synthesis of the anionic complexes $[Fe_2(CO)_6(\mu\text{-CO})_2(\mu\text{-Hg–m})]^-$

$[Fe_2(CO)_8]^{2-}$ displaced a chlorine atom from ClHg–m (m = $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Mn(CO)_5$, $Co(CO)_4$, $Fe(CO)_2Cp$) to afford the mixed metal clusters $[Fe_2(CO)_6(\mu\text{-CO})_2(\mu\text{-Hg–m})]^-$ (Eq. 3).



(eq. 3)

(m = $Mo(CO)_3Cp$ (**1**); $W(CO)_3Cp$ (**2**); $Mn(CO)_5$ (3); $Co(CO)_4$ (4); $Fe(CO)_2Cp$ (**5**))

They were isolated as their NEt_4^+ salts in good yields; all of them are orange, crystalline, and air-unstable solids. They can be manipulated in the air only for a few minutes. In THF solutions **1**–**5** are stable at -20°C for at least 24 h, after which gradual decomposition takes place, giving unidentified products. The instability of these compounds prevented isolation of single crystals for X-ray structure determination. The complexes have been characterized by elemental analyses as well as infrared, ^1H NMR and Mössbauer spectroscopy (Tab. 1). It should be noted that the halide displacement in Eq. 3 gives a product containing an edge-bridged linkage with a three-center two-electron mercury-transition metal bond, rather than a terminal mercury-cluster linkage with a two-center two-electron bond. A reasonable explanation of this behaviour lies in the fact that in a large number of polynuclear compounds the negative charge is thought to be delocalized over two or more metal

Table 1

Analytical and IR spectra data of complexes

Compounds	IR(THF) ν(CO) (cm^{-1})	Analyses Found(calc.)(%) C	H	N	^{1}H NMR (ppm)
1	2020w 1980vs 1960s 1940s 1890m 1875m 1770m	59.20 (60.50)	3.68 (3.69)	1.36 (1.40)	5.39
2	2020w 1975vs 1950vs 1935s 1865m 1770m	29.19 (28.82)	2.70 (2.50)	1.28 (1.40)	5.47
3	2035w 2010m 1985s 1975sh 1935s 1770m	29.23 (29.26)	2.39 (2.32)	1.68 (1.62)	-
4	2025sh 2010m 1980vs 1930s 1880m 1770m	29.68 (29.10)	3.35 (3.09)	2.29 (1.97)	-
5	2020w 1970s 1950sh 1930s 1770m	32.31 (32.73)	3.18 (2.96)	1.72 (1.66)	5.37

centers, thus enabling the formation of compounds with a mercury coordination number greater than two. Several trinuclear ruthenium clusters show a similar behaviour when they are treated with mercury halides [3a], and by this method Shriver has recently obtained the mixed metal cluster (PPN)[$Fe_4(CO)_{13}(\mu$-$HgMo(CO)_3(Cp))$] (PPN = bis(triphenylphosphine)nitrogen(+)) [5]. Interestingly, addition of a further equivalent of ClHg–m to solutions of 1-5 does not produce any change, and the reagents are recovered unaltered. Steric effects probably give rise to the inertness of these mercury clusters.

Formation of the anionic species can be monitored by IR spectroscopy, which shows a shift for the strongest CO stretching band of about 100 cm^{-1} towards higher frequency relative to the band for the starting material, $[Fe_2(CO)_8]^{2-}$. In addition to this, compounds 1-5 show absorptions in the CO bridging group region. The ν(CO) IR pattern for 1-5 is very close to that shown by the similar complex $(NEt_4)[Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}AuPPh_3)]$ (Fig. 1), which has been structurally char-acter&d [6]. This unambiguously confirms the structure proposed for 1-5. These results are not surprising bearing in mind the isolobal analogy between $AuPR_3^+$ and HgR^+ [7]. The ^{57}Fe Mössbauer spectrum of 1 also confirms the proposed structure. Thus, the spectrum shows the expected quadrupole doublet (0.42 mm/s) and the isomer shift (0.11 mm/s) at 80 K corresponds approximately to a -1 charge, as found for the closely related compounds $[PPN]_2[(OC)_4FeEFe(CO)_4]$ (E = Zn, Cd, and Hg) [8].

Remarkably, in no case ligand redistribution could be observed. The final products for such a process would be the *spiro*-type compound $[Hg\{Fe_2(CO)_8\}_2]^{2-}$ and the trimetal complexes m_2Hg. Although the first of these has not yet been obtained, the IR spectra of the latter compounds are well known, and thus their formation in solution would have been easily detected. The IR spectrum of the decomposed solutions even after standing for several hours at room temperature showed no trace of m_2Hg.

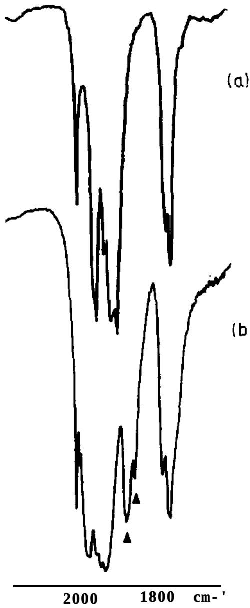
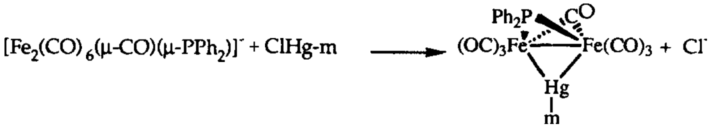


Fig. 1. Infrared spectrum in the ν(CO) region (THF solution) of $(NEt_4)[Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}AuPPh_3)]$ (a), and $(NEt_4)[Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}HgMo(CO)_3(Cp)]$ (b). The bands marked with ▲ correspond to the $Mo(CO)_3(Cp)$ fragment.

In order to make comparisons relative to the ease of ligand redistribution reactions between this type of derivatives and analogous neutral clusters we undertook the synthesis of complexes of formula $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}Hg\text{–}m)]$.

(b) Synthesis of the neutral compounds $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}Hg\text{–}m)]$

The reaction of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ with ClHg–m to give $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}Hg\text{–}m)]$ in THF solution at – 20 ° C was monitored by IR and ^{31}P NMR spectroscopy (Eq. 4).

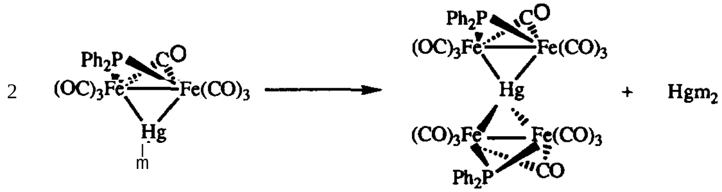


(eq. 4)

(m = $Mo(CO)_3Cp$ (**6**); $W(CO)_3Cp$ (**7**); $Mn(CO)_5$ (**8**); $Co(CO)_4$ (**9**); $Fe(CO)_2Cp$ (**10**))

The IR pattern in the ν(CO) region of compounds 6-10 consists of a number of bands between 2040 and 1900 cm-’ (terminal carbonyl ligands) and one band at 1770 cm-’ (bridging carbonyl group). The close similarity between these spectra and those displayed by the recently obtained complexes $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}MPPh_3)]$ (M = Cu, Ag, and Au) [9], enables us to propose identical geometries for the two compounds and, on the basis of the l&electron rule, a Fe-Fe single bond is required for these compounds to be diamagnetic, electron-precise species. It should be noted that the mixed metal cluster formation from

$[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ is accompanied by a notable shift toward higher frequeny of the band due to the carbonyl bridging group. THF solutions at $-50\,^\circ C$ of derivatives **6–10** showed a simple ^{31}P NMR spectrum consisting of a signal at about -6 ppm (relative to $P(OMe)_3$) along with another invariable signal at 10 ppm, this being particularly intense for m = $Mn(CO)_5$, $Co(CO)_4$ and $Fe(CO)_2Cp$. Remarkably, when the temperature was allowed to raise to $0\,^\circ C$ both signals disappeared with concomitant formation of other peaks at 28 and 46 ppm belonging to unidentified products. These results are interpreted in terms of a process involving the formation of the neutral clusters $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}Hg\text{-}m)]$, which spontaneously redistribute to give the *spiro*-type complex $[Hg\{Fe_2(CO)_7(\mu\text{-}PPh_2)\}_2]$ (signal at + 10 ppm) and m_2Hg (Eq. 5); the latter compounds were easily detected by IR spectroscopy.



(eq. 5)

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In order to confirm this hypothesis we attempted the synthesis of $[Hg\{Fe_2(CO)_7(\mu\text{-}PPh_2)\}_2]$ by reacting $Hg(CN)_2$ with an excess of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ at low temperatures. The signal at + 10 ppm did, indeed, appear, along with the signal at − 13 ppm corresponding to the unreacted phosphido anion. An increase in the temperature led invariably to its rapid decomposition (signals at 28 and 46 ppm). As indicated, the redistribution process is less extensive in the case of the molybdenum complex. These results agree with those recorded for bimetallic complexes involving metal-mercury bonds [2c], although this different behaviour was not clearly understood. The greater stability of 6 towards the ligand redistribution allowed us to isolate it in a pure form in low yield (about 10%) after chromatographic purification.

In conclusion, we have shown that the anionic heterometallic mercury species $[Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}Hg\text{-}m)]^-$ can be isolated as their NEt_4^+ salts in high yields, whereas the neutral derivatives undergo spontaneous metal ligand redistribution reactions. These facts support the idea that these redistribution reactions involve a bimolecular, associative process.

Experimental

Solvents were dried by standard methods and all manipulations and reactions were performed in Schlenk-type flasks under nitrogen. Elemental analyses for C, H, and N were carried out at the Institut de Bio-Orgànica de Barcelona. ^1H NMR and ^{31}P NMR spectra were recorded on a Bruker WP 80SY spectrometer; ^1H shifts are relative to $Si(CH_3)_4$ and ^{31}P shifts are relative to $P(OCH_3)_3$. Infrared spectra were recorded on a Perk&Elmer 1330 spectrophotometer. The Mössbauer spectrum was recorded using a 20mCi of ^{57}Co source in a Rh matrix, and the calibration was with iron foil. Compounds $(NEt_4)_2[Fe_2(CO)_8]$ [10], $ClHgMo(CO)_3Cp$, $ClHgW(CO)_3Cp$,

$ClHgCo(CO)_4$, $ClHgMn(CO)_5$, and $ClHgFe(CO)_2Cp$ [2a] were prepared by procedures described previously.

Synthesis of $(NEt_4)[Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}Hg\text{-}m)]$ (m = $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Fe(CO)_2Cp$, $Mn(CO)_5$, and $Co(CO)_4$)

Details of the synthesis of 1 apply also to 2-5.

A solution of $ClHgMo(CO)_3Cp$ (0.42 g, 0.85 mmol) in THF (25 ml) was added dropwise to a *vigorously stirred* suspension of $(NEt_4)_2[Fe_2(CO)_8]$ (0.51 g, 0.85 mmol) in THF (40 ml) at − 20 ° C; the mixture turned dark red immediately. After 30 min stirring, NEt_4Cl was filtered off and the solvent was reduced to 10ml. 10ml of cold diethyl ether were then added to the filtrate. Red microcrystals were formed when the solution was kept at − 30" C for at least 12 h. After filtration, the microcrystals were washed with a small amount of diethyl ether and dried under vacuum. Yield: 0.65g (80%).

Synthesis of $(NEt_4)[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$

This complex was prepared by a modification of the published method [11]. To a slurry of 2.90 g of $(NEt_4)_2[Fe_2(CO)_8]$ (5 mmol) in 150 ml of THF at 50 ° C, was added 0.82 ml of PPh_2Cl (5 mmol). The solid $(NEt_4)_2[Fe_2(CO)_8]$ dissolved slowly and a red solution was obtained in a few minutes. After 30 min stirring, additional PPh_2Cl (0.2 ml) was added, and the stirring was maintained for another 10 min. After filtration the solution was concentrated to dryness and the solid was treated twice with 30 ml of hexane to remove the excess of phosphine. The resulting red residue was dissolved in CH_2Cl_2 (25 ml) and diethyl ether (20 ml) was added. The red-orange crystals obtained were filtered off, washed with diethyl ether, and dried. Yield: 1.52g, (50%). IR(THF) ν(CO): 2010 m, 1960 vs, 1930 s, 1915 vs, 1710 cm-‘. S ^{31}P NMR: − 13 ppm.

Synthesis of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}HgMo(CO)_3Cp]$

A solution of $ClHgMo(CO)_3Cp$ (0.33g, 0.67 mmol) in THF (20 ml) was added dropwise to a stirred solution of $(NEt_4)[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ (0.42g, 0.67 mmol) in THF (30 ml) at − 20 "C. The solution was allowed to warm to room temperature and then filtered, and the solvent was removed under vacuum. The dark red residue was dissolved in the minimum quantity of THF and adsorbed onto silica. The silica was pumped dry and applied to the top of a chromatography column. Elution with THF-hexane (1 : 1) gave $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}HgMo(CO)_3Cp]$ as a red band, and the product was purified by recrystallization from diethyl ether. Yield: 0.07 g (10%). IR (THF) (ν(CO) cm-‘): 2040 m, 2020 m, I970 vs, 1955 s, 1905 m, 1885 s, 1785w cm-‘. Anal. Found: C, 34.17; H, 1.5. calc: C, 34.53; H, 1.6. S ^{31}P NMR: -6.7 ppm; $^2J(^{31}P\text{-}^{199}Hg)$ = 270 Hz.

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