Polyhedron Vol. 8, No. 12, pp. 1471–1475, 1989
Printed in Great Britain

0277–5387/89 \$3.00+.00

THE INSERTION OF THE $[M(CO)_3(NN)]$ FRAGMENTS ($M = Mo, W$; NN = 2,2′-BIPYRIDINE; 1,10-PHENANTHROLINE; ETHYLENEDIAMINE) INTO THE Hg—X ($X = Cl, Br, I, N_3, SCN$) BONDS OF THE $[\eta^5\text{-}C_5H_5Fe(CO)_2(HgX)]$ COMPLEXES. HETEROTRIMETALLIC COMPOUNDS WITH Fe—Hg—M—X BONDINGS

J. GRANIFO* and M. E. VARGAS

Departamento de Ciencias Químicas, Facultad de Ingeniería y Administración, Universidad de La Frontera, Casilla 54-D, Temuco, Chile

(*Received* 17 *August* 1988; *accepted after revision* 18 *January* 1989)

Abstract—The tricarbonyl complexes $[M(CO)_3(NN)(CH_3CN)]$ ($M = Mo, W$; NN = bipy, phen, en) react with the binuclear complexes $[\eta^5\text{-}C_5H_5Fe(CO)_2(HgX)]$ ($X = Cl, Br, I, SCN, N_3$) to generate trinuclear products of the formula $[\eta^5\text{-}C_5H_5Fe(CO)_2HgM(CO)_3(NN)X]$. These complexes were characterized using IR and electronic spectroscopy. The results are interpreted as the insertion of $M(CO)_3(NN)$ fragments into the Hg—X bonds to give the Fe—Hg—M—X arrays, with the metallic centre, M, being seven-coordinate. The general properties of the new compounds and their reactivity towards monodentate bases and mercury halide derivatives are discussed.

In previous work,[1] we established that the reaction of the $M(CO)_3(NN)$ fragments [$M = Mo, W$; NN = 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen)] with mercury halides, HgX_2 ($X = Cl, Br, I$), can be considered as the insertion of the former between the atoms of the Hg—X bonds to give either bimetallic or trimetallic complexes with X—Hg—M—X and X—M—Hg—M′—X ($M' =$ Mo, W) arrangements, respectively.

In an effort to gain further insight into the factors and conditions determining the insertion behaviour of the $M(CO)_3(NN)$ fragments, we have now studied this reaction with the $[CpFe(CO)_2(HgX)]$ complexes ($Cp = \eta^5\text{-}C_5H_5$; $X = Cl, Br, I, N_3, SCN$).[2] The results of this study show that, in all cases, new trimetallic compounds are obtained, using as the source of the insertion fragments the [*fac*-$M(CO)_3(NN)(CH_3CN)$] complexes.[1]

RESULTS AND DISCUSSION

Treatment of the $[CpFe(CO)_2(HgX)]$ compounds ($X = Cl, Br, I, SCN, N_3$) with $[M(CO)_3(NN)(CH_3CN)]$ ($M = Mo, W$; NN = bipy, phen, en) in methanol at room temperature, affords the heteronuclear trimetal complexes $[CpFe(CO)_2HgM(CO)_3(NN)X]$, according to the reaction:

$$[CpFe(CO)_2(HgX)] + [M(CO)_3(NN)(CH_3CN)] \longrightarrow [CpFe(CO)_2HgM(CO)_3(NN)X] + CH_3CN. \quad (1)$$

The new compounds are air-stable, orange coloured microcrystalline solids. On exposure to sunlight they decompose producing mercury. They are soluble in organic solvents such as methylene chloride, chloroform and acetone; less soluble in alcohols and insoluble in light petroleum. Nevertheless, they are not at all stable in solution.

IR spectra

The IR spectra of the $[CpFe(CO)_2HgM(CO)_3(NN)X]$ complexes in the CO stretching region (Fig. 1, Table 1) show the superimposition of the characteristic patterns of the $CpFe(CO)_2Hg$[2] and $[HgM(CO)_3(NN)X]$ moieties. The last one has been characterized in the $[M(CO)_3(NN)X]_2Hg$[1] and $[M(CO)_3(NN)(X)(HgX)]$ complexes.[1,3] This

---

* Author to whom correspondence should be addressed.

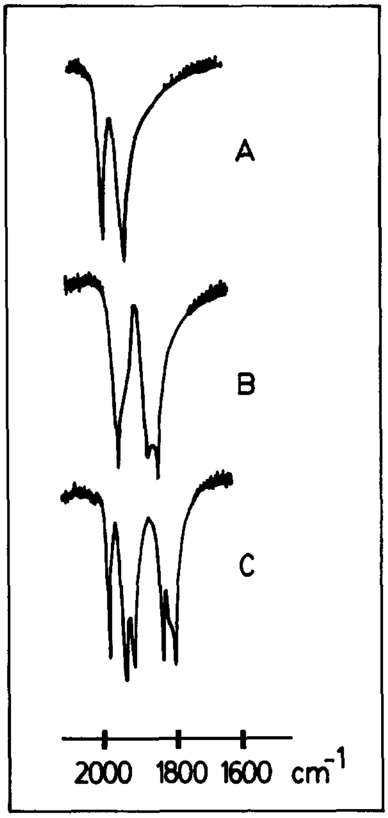

Fig. 1. IR spectra in the ν(CO) region of the complexes: (A) [CpFe(CO)$_2$(HgCl)]. (B) [Mo(CO)$_3$(bipy)(Cl)(HgCl)] and (C) [CpFe(CO)$_2$HgMo(CO)$_3$(bipy)Cl], measured using KBr discs.

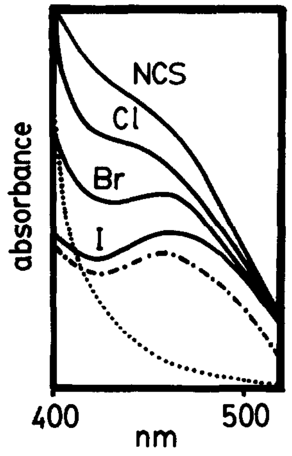

Fig. 2. Visible spectra of [CpFe(CO)$_2$HgMo(CO)$_3$(bipy)X] (——), [CpFe(CO)$_2$HgMo(CO)$_3$(en)Cl] (·····) and [Mo(CO)$_3$(bipy)(Cl)(HgCl)] (—·—·—) complexes in dichloromethane solution.

fact is consistent with the M(CO)$_3$(NN) fragments having been inserted into the Hg—X bonds, giving rise to the Fe—Hg—M—X arrays.

The reaction products of the [CpFe(CO)$_2$HgSCN] complexes with [M(CO)$_3$(NN)(CH$_3$CN)] present the typical IR bands of the N-bonded thiocyanate ligands.[4] More specifically, the ν(CN) stretching vibrations appear near 2070 cm^{-1} and the patterns of the deformation vibrations, δ(NCS), are multiplets centred at *ca* 480 cm^{-1}. The products containing the azido group are characterized by the absorption ν(NN) at *ca* 2050 cm^{-1}. The other IR absorption regions show the presence of bands assignable to all other coordinated ligands.

Electronic absorption spectra in the visible region

The electronic spectra of the [CpFe(CO)$_2$HgM(CO)$_3$(NN)X] complexes in the visible region have been measured in dichloromethane solution. These consist of only one broad band in the 400–490 nm region when NN = bipy or phen, but it is absent if NN = en (Table 1, Fig. 2). The intensity of this band is difficult to assess, as it generally appears on the tail of a much more intense absorption arising from the UV (Fig. 2). Nevertheless, in the [CpFe(CO)$_2$HgM(CO)$_3$(NN)] moiety, this absorption depends on X which is correlated with the spectrochemical series (Table 1), since it is shifted slightly towards the blue region in the sequence I < Br < Cl < NCS. Likewise, the related tricarbonyl complexes [M(CO)$_3$(NN)(X)(HgX)],[3] show comparable spectra (Fig. 2). For instance, their unique band in the visible ($\varepsilon > 3000$ M^{-1} cm^{-1}) is detected only when the π-delocalized bis-chelate ligands, bipy or phen, are present. These antecedents and the fact that the [CpFe(CO)$_2$(HgX)] complexes do not present absorption maxima in the visible, permit us to associate the band between 440 and 490 nm of the [CpFe(CO)$_2$HgM(CO)$_3$(NN)X] complexes with a NN(π^*) $\leftarrow$ M($d\pi$) charge-transfer transition (MLCT).[5]

Reactivity of the [CpFe(CO)$_2$HgM(CO)$_3$(NN)X] *complexes with Lewis bases*

Dissolution of the [CpFe(CO)$_2$HgM(CO)$_3$(NN)X] complexes (M = Mo; NN = bipy, phen; X = Cl, Br, I) in donor solvents such as acetonitrile, produce slow colour changes of the solution from yellow to violet. The MLCT NN(π^*) $\leftarrow$ M($d\pi$) absorption in the visible of the trimetallic complexes is displaced by that of the [Mo(CO)$_3$(NN)(CH$_3$CN)] complexes by *ca* 500 nm.[6] In addition, the UV region shows the superimposition of the bands of the [CpFe(CO)$_2$(HgX)] and [Mo(CO)$_3$(NN)(CH$_3$CN)] complexes. In methylene chloride and in the pres-

Table 1. Analytical, IR and visible spectra for the [CpFe(CO)$_2$HgM(CO)$_3$(NN)X] complexes

Compound			Analysis (%)[a]			IR data (cm^{-1})[b]	Visible spectra (nm)[c]
M	NN	X	C	H	N	ν(CO)	NN(π^*) $\leftarrow$ M($d\pi$)
Mo	bipy	Cl	31.9(32.1)	1.9(1.7)	3.8(3.7)	1991, 1939, 1922, 1842, 1818	450
		Br	30.6(30.3)	1.6(1.7)	3.3(3.5)	1992, 1940, 1918, 1845, 1820	460
		I	28.5(28.6)	1.6(1.6)	3.4(3.3)	1990, 1938, 1915, 1835, 1815	470
		N_3	31.9(31.8)	1.8(1.7)	9.2(9.3)	1990, 1940, 1930, 1840, 1810	[d]
		NCS	32.5(32.7)	1.6(1.7)	5.6(5.4)	1987, 1930, 1925, 1840, 1822	440
	phen	Cl	34.0(34.2)	1.8(1.7)	3.5(3.6)	1990, 1930, 1910, 1838, 1817	445
		Br	32.4(32.3)	1.7(1.6)	3.4(3.4)	1985, 1933, 1916, 1825, 1820	450
		I	30.9(30.6)	1.6(1.5)	3.3(3.2)	1988, 1930, 1918, 1830, 1825	465
		N_3	33.7(33.9)	1.8(1.7)	8.9(9.0)	1988, 1925, 1915, 1830, 1818	[d]
		NCS	34.8(34.7)	1.7(1.6)	5.4(5.3)	1985, 1930, 1920, 1835, 1825	440
	en	Cl	22.0(22.1)	2.1(2.0)	4.2(4.3)	1987, 1930, 1920, 1830, 1815	—
		Br	20.6(20.7)	2.0(1.9)	4.1(4.0)	1985, 1928, 1918, 1833, 1825	—
		I	19.5(19.4)	1.8(1.8)	4.0(3.8)	1986, 1925, 1920, 1830, 1820	—
		N_3	21.7(21.8)	2.1(2.0)	10.5(10.6)	1988, 1926, 1918, 1835, 1822	—
		NCS	23.3(23.1)	1.8(1.9)	6.1(6.2)	1985, 1925, 1916, 1835, 1824	—
W	bipy	Cl	28.8(28.7)	1.7(1.6)	3.5(3.3)	1984, 1920, 1910, 1835, 1815	475
		Br	27.5(27.3)	1.4(1.5)	3.2(3.2)	1984, 1924, 1915, 1833, 1824	485
		I	25.8(25.9)	1.6(1.4)	2.9(3.0)	1987, 1938, 1916, 1834, 1820	495
		N_3	28.6(28.5)	1.5(1.6)	8.5(8.3)	1988, 1933, 1920, 1836, 1824	[d]
		NCS	29.0(29.3)	1.7(1.5)	4.7(4.9)	1990, 1940, 1922, 1834, 1822	465
	phen	Cl	30.7(30.7)	1.6(1.5)	3.4(3.3)	1988, 1938, 1925, 1830, 1810	470
		Br	29.3(29.2)	1.5(1.4)	3.2(3.1)	1985, 1936, 1915, 1830, 1820	480
		I	27.9(27.7)	1.4(1.4)	2.8(2.9)	1987, 1935, 1918, 1835, 1820	490
		N_3	30.7(30.5)	1.6(1.5)	8.3(8.1)	1988, 1938, 1930, 1835, 1810	[d]
		NCS	31.1(31.3)	1.5(1.5)	5.0(4.8)	1987, 1935, 1925, 1822, 1818	460
	en	Cl	19.4(19.5)	1.9(1.8)	3.9(3.8)	1990, 1938, 1925, 1825, 1820	—
		Br	18.5(18.4)	1.6(1.7)	3.7(3.6)	1986, 1933, 1920, 1835, 1820	—
		I	17.2(17.3)	1.7(1.6)	3.4(3.4)	1988, 1937, 1923, 1838, 1822	—
		N_3	19.5(19.3)	1.8(1.8)	9.6(9.4)	1990, 1936, 1920, 1840, 1825	—
		NCS	20.1(20.4)	1.6(1.7)	5.7(5.5)	1990, 1938, 1925, 1835, 1820	—

[a] Required values are given in parentheses.

[b] KBr discs, all bands are strong.

[c] In CH_2Cl_2.

[d] Complex is too unstable in solution.

ence of an excess of monodentate base, such as triphenylphosphine or tetramethylthiourea, the trimetallic complexes react in a similar way to when they are in acetonitrile, giving solutions containing the [CpFe(CO)$_2$(HgX)] and [Mo(CO)$_3$(NN)L] complexes. These results suggest the existence of the equilibrium (L = donor solvent or monodentate bases):

$$[\mathrm{CpFe(CO)_2HgMo(CO)_3(NN)X}] + \mathrm{L} \longrightarrow [\mathrm{CpFe(CO)_2(HgX)}] + [\mathrm{Mo(CO)_3(NN)L}]. \quad (2)$$

The reaction rate of the [CpFe(CO)$_2$HgMo(CO)$_3$(NN)X] complexes with acetonitrile was measured following the absorbance increase at 500 nm. The plots of $\ln(A - A_\infty)$ vs t yield straight lines indicating a first- or pseudo-first-order kinetic law. The rate constants depend on the electronegativity of the halide and increase in the sequence Cl($k_{obs} = 0.1$ s^{-1}) < Br($k_{obs} = 1$ s^{-1}) < I(k_{obs} greater than 1 s^{-1}). When X = NCS or N_3 this reaction does not take place. Then, a plausible explanation for these results might be related mainly to the net electronic density upon the hepta-coordinate molybdenum atom.

The inert character of the [CpFe(CO)$_2$M(CO)$_3$(NN)X] complexes (M = W) can probably be attributed to the softer character of the tungsten atom.

Exchange reactions with mercuric halides

The [CpFe(CO)$_2$HgM(CO)$_3$(NN)Cl] complexes (M = Mo, W; NN = bipy, phen) react in acetone with HgCl$_2$. The characteristics of the reaction depend on the stoichiometric proportions of the reactants. If it is 1 : 1, the colour of the solution changes rapidly from orange to yellow, but if it is 2 : 1, then, besides the colour change, the symmetric trimetallic complexes [M(CO)$_3$(NN)Cl]$_2$Hg[1] are precipitated, while in solution the presence of the compound [CpFe(CO)$_2$(HgCl)] is detected. These results suggest the occurrence of the following exchange reactions:

$$[\mathrm{CpFe(CO)_2HgM(CO)_3(NN)Cl}] + \mathrm{HgCl_2} \longrightarrow [\mathrm{CpFe(CO)_2HgCl}] + [\mathrm{M(CO)_3(NN)(HgCl)Cl}] \quad (3)$$

$$[\mathrm{CpFe(CO)_2HgM(CO)_3(NN)Cl}] + [\mathrm{M(CO)_3(NN)(HgCl)Cl}] \longrightarrow [\mathrm{CpFe(CO)_2(HgCl)}] + [\mathrm{M(CO)_3(NN)Cl}]_2\mathrm{Hg}. \quad (4)$$

In the first step, an exchange process involving the trimetallic complex [CpFe(CO)$_2$HgM(CO)$_3$(NN)Cl] and mercuric chloride occurs, giving the soluble complexes [CpFe(CO)$_2$(HgCl)] and [M(CO)$_3$(NN)Cl(HgCl)Cl] [eq. (3)]. This last product, in its own time, exchanges with a second molecule of the initial complex yielding a solution containing the [CpFe(CO)$_2$(HgCl)] complex and the insoluble compound [M(CO)$_3$(NN)Cl]$_2$Hg [eq. (4)].

The verification of the above exchange reaction sequence was made by involving the [CpFe(CO)$_2$HgM(CO)$_3$(NN)Cl] and [M(CO)$_3$(NN)(HgCl)Cl] complexes in the reaction. The formation of the products indicated in eq. (4) was observed. Further evidence was gained when by this same process it was possible to isolate the asymmetric trimetallic complexes M′—Hg—M′[1] (M′ = Mo, W; NN = bipy, phen):

$$[\mathrm{CpFe(CO)_2HgM(CO)_3(NN)Cl}] + [\mathrm{M'(CO)_3(NN')(HgCl)Cl}] \longrightarrow [\mathrm{CpFe(CO)_2(HgCl)}] + [\mathrm{Cl(NN)(CO)_3MHgM'(CO)_3(NN')Cl}]. \quad (5)$$

The [CpFe(CO)$_2$HgM(CO)$_3$(NN)Cl] complexes with NN = en, undergo the same reactions, but no noticeable colour changes of the solutions are observed due to the absence of the NN(π^*) ← M($d\pi$) band.

EXPERIMENTAL

The solvents were purified by standard methods and all operations were carried out under a nitrogen atmosphere. The starting materials, M(CO)$_4$(NN),[7,8] [M(CO)$_3$(NN)(CH$_3$CN)],[9] [M(CO)$_3$(NN)(X)(HgX)][1,3] and [CpFe(CO)$_2$(HgX)],[2] (M = Mo, W; NN = bipy, phen, en; X = Cl, Br, I), were prepared by similar methods to those described in the literature. The [CpFe(CO)$_2$(HgX)] complexes (X = N$_3$, SCN) were precipitated by treating an acetonitrile solution of [CpFe(CO)$_2$(HgCl)] with an excess of the NaX salt dissolved in water; the yellow crystals were filtered off and washed with water. The IR spectra were obtained by means of a Perkin–Elmer 577 spectrophotometer. The electronic spectra were recorded on a Carl–Zeiss DMR 22 instrument.

Synthesis of [CpFe(CO)$_2$HgM(CO)$_3$(NN)X] (Cp = η^5-C$_5$H$_5$; M = Mo, W; NN = bipy, phen, en; X = Cl, Br, I, SCN, N$_3$)

These compounds were synthesized by reaction of the [M(CO)$_3$(NN)(CH$_3$CN)] and [CpFe(CO)$_2$(HgX)] complexes in methanol. All these substances were orange microcrystalline solids. The following preparation is described as a typical one.

[CpFe(CO)$_2$HgMo(CO)$_3$(en)Cl]. A mixture of 0.304 g (0.736 mmol) of [CpFe(CO)$_2$(HgCl)] and 0.207 g (0.736 mmol) of freshly prepared [Mo(CO)$_3$(en)(CH$_3$CN)] was vigorously stirred in 10 cm^3 of methanol in the dark for 0.5 h. The bright orange precipitate was filtered and washed 3–4 times with 3 cm^3 portions of methanol. 0.394 g (82% yield) of the microcrystalline compound were obtained. The elemental analyses of these compounds are given in Table 1.

Acknowledgements—Financial support given by the Dirección de Investigación de la Universidad de La Frontera (Project N° 1032126) to carry out this work is gratefully acknowledged. Also, we thank Miss J. Navarro, Miss A. Videla and Miss E. Klein (USACH) for their helpful assistance.

REFERENCES

1. P. Correa, M. E. Vargas and J. Granifo, *Polyhedron* 1987, **6**, 1781.
2. M. J. Mays and J. D. Robb, *J. Chem. Soc. A* 1968, 329; R. Kumar, A. R. Manning and P. T. Murray, *J. Organomet. Chem.* 1987, **323**, 53.
3. K. E. Edgar, B. F. G. Johnson, J. Lewis and S. B. Wild, *J. Chem. Soc. A* 1968, 2851.

4. D. M. Adams, *Metal Ligand and Related Vibrations*, p. 327. E. Arnold, London (1967).
5. H. Saito, J. Fujita and K. Saito, *Bull. Chem. Soc. Jpn* 1968, **41**, 359, 863.
6. J. Granifo, M. E. Vargas, J. Costamagna and M. A. François, *Polyhedron* 1988, **7**, 489.
7. M. H. B. Stiddard, *J. Chem. Soc.* 1962, 4712.
8. C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.* 1963, **2**, 533.
9. L. W. Houk and G. R. Dobson, *Inorg. Chem.* 1965, **5**, 2119.