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Insertion of mercury into iron–iodine bonds leading to dinuclear (Fe–Hg) mixed isonitrile–phosphine complexes

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Abstract

The binuclear complexes *trans*-[Fe(HgI₂)(PPh₃)(CNR)₄] (R = Ph, 4-MeC₆H₄, or ^tBu), *trans*-[Fe(HgI₂)(dppm-P)(CNR)₄] (R = Ph or 4-MeC₆H₄), and *mer*-[Fe(HgI₂)(dppe)(CNR)₃] (R = Ph or 4-MeC₆H₄) were obtained by the reaction of metallic mercury with [FeI₂(CNR)₄] in the presence of phosphines such as PPh₃, Ph₂PCH₂PPh₂ (dppm) and Ph₂PCH₂CH₂PPh₂ (dppe); this process yields adducts of the Lewis acid HgI₂ with the metallic bases “FeL(CNR)₄” (L = PPh₃ or dppm-P) or “Fe(dppe)(CNR)₃”. Spectroscopic data and conductivity measurements suggest a sequence for the strength of these metallic fragments acting as bases.

Key words: Iron; Mercury; Isonitrile; Phosphine

1. Introduction

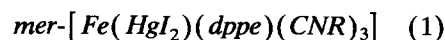
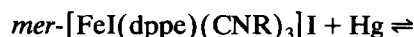
Heterometallic complexes containing mercury bonded to transition metals are well known [1,2], although there are very few examples of the insertion of metallic mercury into metal–halogen bonds [3]. Recently we have reported the syntheses of [(RNC)₅Fe → HgI₂] (1) (R = Ph, 4-MeC₆H₄, or ^tBu) by reaction of Hg and [FeI₂(CNR)₄] in the presence of an additional equivalent of isonitrile [4]. Here we extend this study to the reactions of mercury with *cis*- or *trans*-[FeI₂(CNR)₄] (R = Ph, 4-MeC₆H₄, or ^tBu) when phosphines such as PPh₃, dppm and dppe are present yielding new heterometallic dinuclear (Fe → Hg) mixed isonitrile-phosphine derivatives.

2. Results and discussion

The addition of mercury to a solution of either *cis*- or *trans*-[FeI₂(CNR)₄] (R = Ph, 4-MeC₆H₄, or ^tBu), and an equimolar amount of PPh₃ gives *trans*-[Fe(HgI₂)(PPh₃)(CNR)₄] (2) (i, Scheme 1) which may be regarded as metal donor–acceptor complexes [4]. The IR spectra (Table 1), indicate a *trans* arrangement

[5], and 2c shows $\nu(\text{C}\equiv\text{N})$ at higher average frequency than that reported for its related free base “Fe(PPh₃)(CN^tBu)₄” [6], reflecting the decrease of the electron density at the iron atom produced by its coordination to HgI₂. The ¹H NMR and ³¹P{¹H} NMR spectra (Table 2) are consistent with the proposed geometry and the values of the coupling constants, ²J(Hg–P), imply a *trans* structure [7].

The insertion reaction also occurs with diphosphines (dppm or dppe) (ii, iii, Scheme 1) giving *trans*-[Fe(HgI₂)(dppm-P)(CNR)₄] (3) and *mer*-[Fe(HgI₂)(dppe)(CNR)₃] (4) (R = Ph or 4-MeC₆H₄). However, this is not a straightforward method to obtain 3 and 4 since *mer*-[FeI(diphos)(CNR)₃]I is always also formed [8] in similar amounts, and attempts to purify them failed. Analogously, the direct treatment of *mer*-[FeI(dppe)(CNR)₃]I (R = Ph or 4-MeC₆H₄) with an excess of mercury in THF during 24 h at room temperature gives the mixture of the inserted and cationic species, suggesting the equilibrium (1).



Fortunately, 3 and 4 are cleanly obtained when [(RNC)₅Fe–HgI₂] (1) (R = Ph or 4-MeC₆H₄) react with a three-fold excess of diphosphine in refluxing

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THF (v, vi, Scheme 1). Attempts to extend this last method to the CN^tBu derivatives were unsuccessful. Thus reaction of $[(^t\text{BuNC})_5\text{Fe–HgI}_2]$ with dppm produced mercury, *mer*- $[\text{FeI}(\text{dppm})(\text{CN}^t\text{Bu})_3]\text{I}$ (see Experimental section), and possibly *trans*- $[\text{Fe}(\text{HgI}_2)(\text{dppm-}P)(\text{CN}^t\text{Bu})_4]$, characterized by a singlet in its ^1H NMR spectrum at 1.66 δ .

Monodentate coordination of dppm in **3** is evident from their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Table 2) [8,9], and their ^1H NMR and the IR spectra are similar to those from **2** indicating a *trans* arrangement. The IR spectra of complexes **4** (Table 1), indicate a *mer* disposition of the isonitriles [5,8], with **4a** having an average frequency for $\nu(\text{C}\equiv\text{N})$ higher than that of its related free base “ $\text{Fe}(\text{dppe})(\text{CNPh})_3$ ” [10]. The high field doublet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Table 2) is assigned to the phosphorus *trans* to the isonitrile group [8,11].

Compounds **2** and **3** are non-conductors in nitrobenzene whereas **4** are 1:1 electrolytes [12]. These results

are consistent [4] with the greater basicity of the iron fragment causing dissociation of iodide. These results allow us to establish a sequence of the metallic base strength towards HgI_2 for $\text{R} = \text{Ph}$ or $4\text{-MeC}_6\text{H}_4$: “ $\text{Fe}(\text{dppe})(\text{CNR})_3$ ” > “ $\text{Fe}(\text{dppm-}P)(\text{CNR})_4$ ” $\approx$ “ $\text{Fe}(\text{PPh}_3)(\text{CNR})_4$ ”. This strongly supports the inference of equilibrium (1), and explains the failure to obtain **3** and **4** when $\text{R} = ^t\text{Bu}$.

3. Experimental details

3.1. General

All reactions were performed under dinitrogen following routine procedures. Microanalyses (C, H, N) were performed by Centro de Investigación y Desarrollo-C.S.I.C. Barcelona (Spain). I.R. data (P.E. 593 or 883 spectrometers) are collected in Table 1 and ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Bruker AC 80) in Table 2. Literature methods were used to prepare

TABLE 1. Analytical and infrared data for complexes **2a–4b**

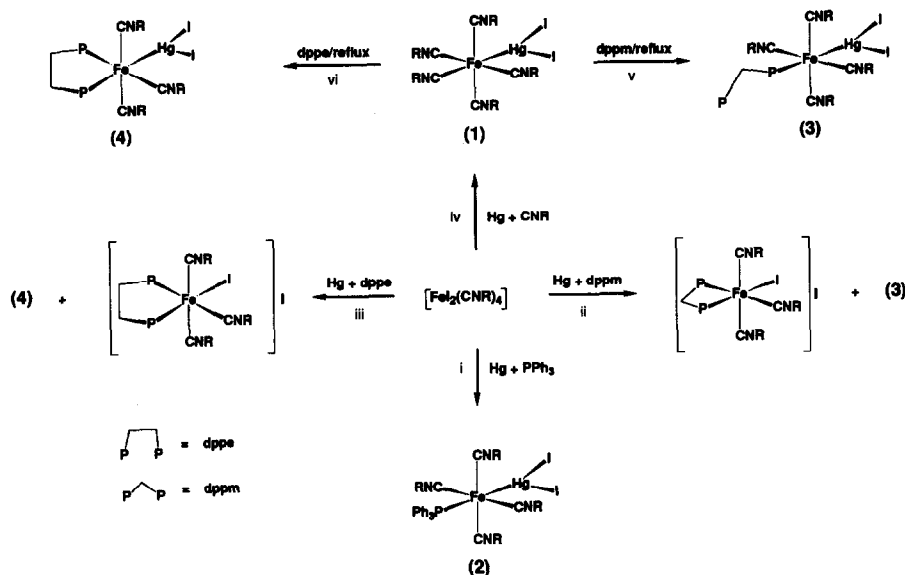
Compound	Elemental analysis (%) ^a			IR (cm^{-1})	
	C	H	N	$\nu(\text{C}\equiv\text{N})/\text{CH}_2\text{Cl}_2$	$\nu(\text{C}\equiv\text{N})/\text{Nujol}$
2a $[\text{Fe}(\text{HgI}_2)(\text{PPh}_3)(\text{CNPh})_4]$	46.31 (46.62)	2.84 (2.95)	5.02 (4.72)	2098s	2095s
2b $[\text{Fe}(\text{HgI}_2)(\text{PPh}_3)(\text{CNC}_6\text{H}_4\text{CH}_3\text{-}4)_4]$	47.86 (48.38)	3.22 (3.46)	4.70 (4.51)	2100s	2090s 2035w(sh)
2c $[\text{Fe}(\text{HgI}_2)(\text{PPh}_3)(\text{CN}^t\text{Bu})_4]$	41.53 (41.30)	5.05 (5.07)	4.56 (4.61)	2120s	2110s 2050w(sh)
3a $[\text{Fe}(\text{HgI}_2)(\text{dppm-}P)(\text{CNPh})_4]$	49.01 (48.69)	3.35 (3.21)	4.16 (4.28)	2105s	2085s
3b $[\text{Fe}(\text{HgI}_2)(\text{dppm-}P)(\text{CNC}_6\text{H}_4\text{CH}_3\text{-}4)_4]$	50.83 (50.21)	3.72 (3.67)	4.30 (4.11)	1100s	2090s 2040w(sh)
4a $[\text{Fe}(\text{HgI}_2)(\text{dppe})(\text{CNPh})_3]$	45.84 (46.34)	3.36 (3.20)	3.29 (3.45)	2135w(sh) 2095s	2125w 2085s
4b $[\text{Fe}(\text{HgI}_2)(\text{dppe})(\text{CNC}_6\text{H}_4\text{CH}_3\text{-}4)_3]$	49.79 (47.65)	3.87 (3.57)	3.40 (3.33)	2145w 2092s	2119w 2092s

^a Calculated values in parentheses. Abbreviations: s, strong; sh, shoulder; w, weak.

TABLE 2. NMR data (CDCl_3) for complexes **2a–4b**

Compound	^1H ^a	$^{31}\text{P}\{^1\text{H}\}$ ^a
2a	7.06–7.89 (aromatic)	59.7 (s, $^2J(\text{P–Hg}) = 857$)
2b	2.16 (s, 12H, CH_3); 6.67–7.79 (31H, aromatic)	60.3 (s, $^2J(\text{P–Hg}) = 911$)
2c	1.35 (s, 36H, $\text{C}(\text{CH}_3)_3$); 7.10–7.54 (15H, aromatic)	61.9 (s, $^2J(\text{P–Hg}) = 982$)
3a	3.57 (dd, 2H, $J(\text{P–H}) = 7.8$ and 1); 6.86–7.85 (40H, aromatic)	52.0 (d, $^2J(\text{P–Hg}) = 827$); $-28.5(\text{d})$; ($^2J(\text{P–P}) = 76$)
3b	2.30 (s, 12H, CH_3); 3.40 (dd, 2H, $J(\text{P–H}) = 7.9$ and 1); 6.96–7.67 (36H, aromatic)	52.9 (d, $^2J(\text{P–Hg}) = 868$); $-27.8(\text{d})$; ($^2J(\text{P–P}) = 71$)
4a	3.04 (m, 4H, CH_2); 6.65–7.87 (35H, aromatic)	81.3 (d, $^2J(\text{P–Hg}) = 804$); 78.8 (d, $^2J(\text{P–Hg}) = 778$); ($^2J(\text{P–P}) = 11$)
4b	2.09 (s, 6H, CH_3); 2.16 (s, 3H, CH_3); 2.98 (m, 4H, CH_2); 6.30–7.80 (32H, aromatic)	84.8 (d, $^2J(\text{P–Hg}) = 785$); 82.0 (d, $^2J(\text{P–Hg}) = 774$); ($^2J(\text{P–P}) = 11$)

^a Shifts in ppm downfield relative to internal TMS (^1H) or external 85% H_3PO_4 in H_2O (^{31}P); coupling constants in Hz. Abbreviations: s, singlet; d, doublet; dd, doublet of doublets; m, multiplet.



Scheme 1. For (i) and (iv), R = Ph, 4-MeC₆H₄, or ^tBu. For (ii), (iii), (v) and (vi), R = Ph or 4-MeC₆H₄. Reactions carried out in THF at room temperature unless otherwise indicated.

CNR (R = Ph, 4-MeC₆H₄, or ^tBu) [13], [FeI₂(CNR)₄] [14], *mer*-[FeI(diphos)(CNR)₃]I (diphos = dppm or dppe) [8], [(RNC)₅Fe–HgI₂] (R = Ph, 4-MeC₆H₄, or ^tBu) [4], dppm [15], and dppe [16]. PPh₃ was purchased (Maybridge, UK) and used without further purification and mercury metal was used after distillation.

3.2. Preparation of *mer*-[Fe(I)(dppm)(CN^tBu)₃]I

This new compound was prepared following the method described for other *mer*-[Fe(I)(diphos)(CNR)₃]I [8]. Anal. Found: C, 50.64; H, 5.18; N, 4.87. C₄₀H₄₉FeI₂N₃P₂ calc.: C, 50.92; H, 3.28; N, 4.45%. ¹H NMR (CDCl₃): δ 1.04 (s, 18H, C(CH₃)₃); 1.76 (s, 9H, C(CH₃)₃); 5.39 (t, 2H, CH₂; J(PH) = 11.4 Hz); 7.30–7.66 (20H, aromatic). IR (CHCl₃): ν(C≡N): 2184w; 2150s cm⁻¹.

3.3. Preparation of complexes 2

Metallic mercury (10 g) was added to a solution of [FeI₂(CNPh)₄] (0.300 g, 0.417 mmol) and triphenylphosphine (0.158 g, 0.603 mmol) in THF (20 cm³). After stirring at room temperature for 20 h the excess of mercury was separated, and the solution filtered on kieselguhr. The solvent was pumped off and the oily residue stirred in toluene until it completely transformed into an orange powder. Recrystallization from CH₂Cl₂/ethanol (1:1) afforded yellow-orange air-stable crystals of **2a** (0.210 g, 43% yield). Compounds **2b** (58%) and **2c** (44%) were obtained similarly.

3.4. Preparation of complexes 3 and 4

A stirred mixture of [(PhNC)₅Fe–HgI₂] (0.300 g, 0.292 mmol) and dppm (0.500 g, 1.302 mmol) in THF

(50 cm³) was heated under reflux for 8 h. The solvent was removed under reduced pressure and the oily residue washed with toluene (2 × 15 cm³) and diethylether (2 × 15 cm³) to remove the excess of phosphine. Recrystallization from CH₂Cl₂/ethanol afforded orange crystals of **3a** (0.210 g, 43% yield). **3b** (47%), **4a** (64%) and **4b** (37%) were obtained similarly as orange air-stable crystals.

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