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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(HgI$_2$)(PPh$_3$)(CNR)$_4$] (R = Ph, 4-MeC$_6$H$_4$, or ^{t}Bu), *trans*-[Fe(HgI$_2$)(dppm-*P*)(CNR)$_4$] (R = Ph or 4-MeC$_6$H$_4$), and *mer*-[Fe(HgI$_2$)(dppe)(CNR)$_3$] (R = Ph or 4-MeC$_6$H$_4$) were obtained by the reaction of metallic mercury with [FeI$_2$(CNR)$_4$] in the presence of phosphines such as PPh$_3$, Ph$_2$PCH$_2$PPh$_2$ (dppm) and Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe); this process yields adducts of the Lewis acid HgI$_2$ with the metallic bases "FeL(CNR)$_4$" (L = PPh$_3$ 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)$_5$Fe → HgI$_2$] (**1**) (R = Ph, 4-MeC$_6$H$_4$, or ^{t}Bu) by reaction of Hg and [FeI$_2$(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*-[FeI$_2$-(CNR)$_4$] (R = Ph, 4-MeC$_6$H$_4$, or ^{t}Bu) when phosphines such as PPh$_3$, 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*-[FeI$_2$(CNR)$_4$] (R = Ph, 4-MeC$_6$H$_4$, or ^{t}Bu), and an equimolar amount of PPh$_3$ gives *trans*-[Fe(HgI$_2$)(PPh$_3$)(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 ν(C≡N) at higher average frequency than that reported for its related free base "Fe(PPh$_3$)-(CN^{t}Bu)$_4$" [6], reflecting the decrease of the electron density at the iron atom produced by its coordination to HgI$_2$. The ^{1}H NMR and ^{31}P{^{1}H} 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(HgI$_2$)(dppm-*P*)(CNR)$_4$] (**3**) and *mer*-[Fe(HgI$_2$)(dppe)(CNR)$_3$] (**4**) (R = Ph or 4-MeC$_6$H$_4$). 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-MeC$_6$H$_4$) 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).

$$mer\text{-}[\mathrm{FeI(dppe)(CNR)_3}]\mathrm{I} + \mathrm{Hg} \rightleftharpoons mer\text{-}[Fe(HgI_2)(dppe)(CNR)_3] \quad (1)$$

Fortunately, **3** and **4** are cleanly obtained when [(RNC)$_5$Fe–HgI$_2$] (**1**) (R = Ph or 4-MeC$_6$H$_4$) 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^{t}Bu derivatives were unsuccessful. Thus reaction of [(^{t}BuNC)$_5$Fe–HgI$_2$] with dppm produced mercury, *mer*-[FeI(dppm)(CN^{t}Bu)$_3$]I (see Experimental section), and possibly *trans*-[Fe(HgI$_2$)(dppm-*P*)(CN^{t}Bu)$_4$], characterized by a singlet in its ^{1}H NMR spectrum at 1.66 δ.

Monodentate coordination of dppm in **3** is evident from their ^{31}P{^{1}H} NMR spectra (Table 2) [8,9], and their ^{1}H 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 ν(C≡N) higher than that of its related free base "Fe(dppe)(CNPh)$_3$" [10]. The high field doublet in the ^{31}P{^{1}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 R = Ph or 4-MeC$_6$H$_4$: "Fe(dppe)(CNR)$_3$" > "Fe(dppm-*P*)(CNR)$_4$" ≈ "Fe(PPh$_3$)(CNR)$_4$". This strongly supports the inference of equilibrium (1), and explains the failure to obtain **3** and **4** when R = ^{t}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 ^{1}H NMR and ^{31}P{^{1}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**

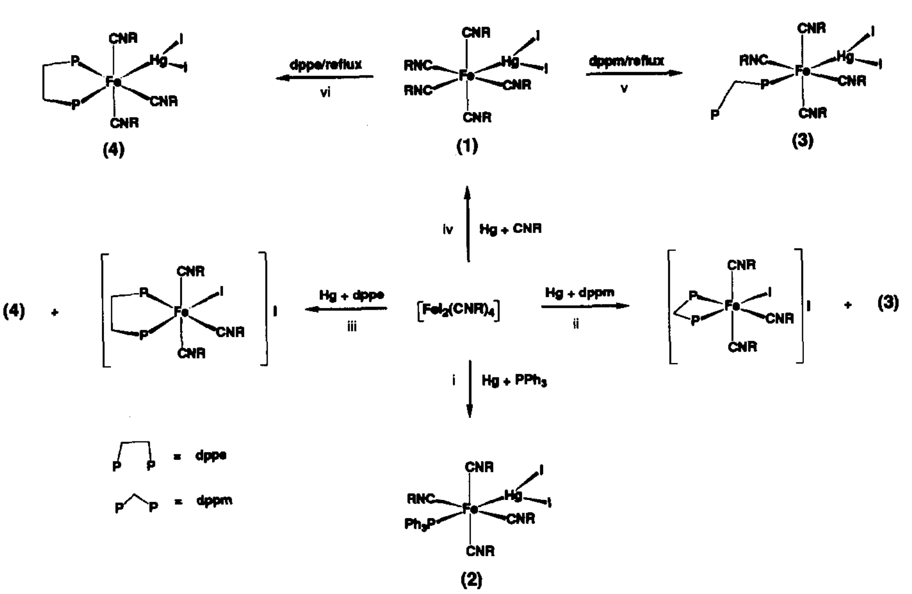
Compound	Elemental analysis (%) [a]			IR (cm^{-1})	
	C	H	N	ν(C≡N)/CH$_2$Cl$_2$	ν(C≡N)/Nujol
2a [Fe(HgI$_2$)(PPh$_3$)(CNPh)$_4$]	46.31 (46.62)	2.84 (2.95)	5.02 (4.72)	2098s	2095s
2b [Fe(HgI$_2$)(PPh$_3$)(CNC$_6$H$_4$CH$_3$-4)$_4$]	47.86 (48.38)	3.22 (3.46)	4.70 (4.51)	2100s	2090s 2035w(sh)
2c [Fe(HgI$_2$)(PPh$_3$)(CN^{t}Bu)$_4$]	41.53 (41.30)	5.05 (5.07)	4.56 (4.61)	2120s	2110s 2050w(sh)
3a [Fe(HgI$_2$)(dppm-*P*)(CNPh)$_4$]	49.01 (48.69)	3.35 (3.21)	4.16 (4.28)	2105s	2085s
3b [Fe(HgI$_2$)(dppm-*P*)(CNC$_6$H$_4$CH$_3$-4)$_4$]	50.83 (50.21)	3.72 (3.67)	4.30 (4.11)	1100s	2090s 2040w(sh)
4a [Fe(HgI$_2$)(dppe)(CNPh)$_3$]	45.84 (46.34)	3.36 (3.20)	3.29 (3.45)	2135w(sh) 2095s	2125w 2085s
4b [Fe(HgI$_2$)(dppe)(CNC$_6$H$_4$CH$_3$-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	^{1}H [a]	^{31}P{^{1}H} [a]
2a	7.06–7.89 (aromatic)	59.7 (s, ^2J(P–Hg) = 857)
2b	2.16 (s, 12H, CH$_3$); 6.67–7.79 (31H, aromatic)	60.3 (s, ^2J(P–Hg) = 911)
2c	1.35 (s, 36H, C(CH$_3$)$_3$); 7.10–7.54 (15H, aromatic)	61.9 (s, ^2J(P–Hg) = 982)
3a	3.57 (dd, 2H, J(P–H) = 7.8 and 1); 6.86–7.85 (40H, aromatic)	52.0 (d, ^2J(P–Hg) = 827); −28.5(d); (^2J(P–P) = 76)
3b	2.30 (s, 12H, CH$_3$); 3.40 (dd, 2H, J(P–H) = 7.9 and 1); 6.96–7.67 (36H, aromatic)	52.9 (d, ^2J(P–Hg) = 868); −27.8 (d); (^2J(P–P) = 71)
4a	3.04 (m, 4H, CH$_2$); 6.65–7.87 (35H, aromatic)	81.3 (d, ^2J(P–Hg) = 804); 78.8 (d, ^2J(P–Hg) = 778); (^2J(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(P–Hg) = 785); 82.0 (d, ^2J(P–Hg) = 774); (^2J(P–P) = 11)

[a] Shifts in ppm downfield relative to internal TMS (^{1}H) or external 85% H$_3$PO$_4$ in H$_2$O (^{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-MeC_6H_4, or ^{t}Bu. For (ii), (iii), (v) and (vi), R = Ph or 4-MeC_6H_4. Reactions carried out in THF at room temperature unless otherwise indicated.

CNR (R = Ph, 4-MeC_6H_4, or ^{t}Bu) [13], [FeI_2(CNR)$_4$] [14], *mer*-[FeI(diphos)(CNR)$_3$)]I (diphos = dppm or dppe) [8], [(RNC)$_5$Fe-HgI_2] (R = Ph, 4-MeC_6H_4, or ^{t}Bu) [4], dppm [15], and dppe [16]. PPh_3 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^{t}Bu)$_3$]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. $C_{40}H_{49}FeI_2N_3P_2$ calc.: C, 50.92; H, 3.28; N, 4.45%. ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 18H, C(CH_3)$_3$); 1.76 (s, 9H, C(CH_3)$_3$); 5.39 (t, 2H, CH_2; *J*(PH) = 11.4 Hz); 7.30–7.66 (20H, aromatic). IR ($CHCl_3$): ν(C≡N): 2184w; 2150s cm^{-1}.

3.3. Preparation of complexes 2

Metallic mercury (10 g) was added to a solution of [FeI_2(CNPh)$_4$] (0.300 g, 0.417 mmol) and triphenylphosphine (0.158 g, 0.603 mmol) in THF (20 cm^3). 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 CH_2Cl_2/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)$_5$Fe–HgI_2] (0.300 g, 0.292 mmol) and dppm (0.500 g, 1.302 mmol) in THF (50 cm^3) was heated under reflux for 8 h. The solvent was removed under reduced pressure and the oily residue washed with toluene (2 × 15 cm^3) and diethylether (2 × 15 cm^3) to remove the excess of phosphine. Recrystallization from CH_2Cl_2/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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References

1 J.M. Burlitch, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. VI, Pergamon Press, Oxford 1982, p. 983.
2 See for example: (a) P. Braunstein, J. Calvet, O. Rosell and M. Seco, *J. Chem. Soc. Dalton Trans.*, (1987) 119; (b) E. Rosenberg, K. King, R. Fahmy and A. Tiripicchio, *J. Am. Chem. Soc.*, *102* (1980) 3626.
3 (a) A.N. Nesmeyanov, L.G. Makarova and V.N. Vinogradova, *Izv. Akad. Nauk SSSR, Ser Khim.*, (1969) 1398; (b) A.N. Nesmeyanov, L.G. Makarova and V.N. Vinogradova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1972) 122.
4 S. Coco, P. Espinet, F. Mayor and X. Solans, *J. Chem. Soc., Dalton Trans.*, (1991) 2503.
5 G. Albertin, E. Bordignon, S. Calogero, A.A. Orio and G. Pelizzi, *J. Organomet. Chem.*, *157* (1978) 51.
6 J.M. Bassett, D.E. Berry, G.K. Barker, M. Green, J.A.K. Howard and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1979) 1003.
7 J.A. Statler, G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1984) 1731.

8 V. Riera, J. Ruiz and F. Mayor, *J. Organomet. Chem.*, *276* (1984) 47.
9 (a) P. Braunstein, M. Knorr, V. Schubert, M. Lanfrachi and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, (1991) 1507; (b) G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, (1987) 1509.
10 V. Riera, J. Ruiz, Y. Jeannin and M. Philoche-Levisalles, *J. Chem. Soc., Dalton Trans.*, (1988) 1591.
11 G. Balimann and P.S.J. Pregosin, *Magn. Reson.*, *22* (1976) 235.
12 W.J. Geary, *Coord. Chem. Rev.*, *7* (1971) 81.
13 W.P. Weber, G.W. Gokel and I.K. Ugi, *Angew. Chem., Int. Ed. Engl.*, *11* (1972) 530.
14 L. Malatesta and F. Bonati, *Isocyanide Complexes of Metals*, Wiley, New York, 1969.
15 A.M. Aguiar and J. Beisler, *J. Organomet. Chem.*, *29* (1964) 1660.
16 J. Chatt and F.A. Hart, *J. Chem. Soc.*, (1960) 1378.