Cite this: Dalton Trans., 2011, 40, 4722

PAPER

The coordination behaviour of ferrocene-based pyridylphosphine ligands towards $Zn^{II},\,Cd^{II}$ and $Hg^{II}\dagger\ddagger$

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Received 22nd December 2010, Accepted 17th February 2011 DOI: 10.1039/c0dt01810d

The reaction of Group 12 metal dihalides MX_2 with the *P*,*N*-ligands [Fe(C₅H₄-PPh₂)(C₅H₄-2-py)] (1) (2-py = pyrid-2-yl), [Fe(C₅H₄-PPh₂)(C₅H₄-CH₂-2-py)] (2) and [Fe(C₅H₄-PPh₂)(C₅H₄-3-py)] (3) (3-py = pyrid-3-yl) was investigated. For a 1 : 1 molar ratio of MX_2 and the respective ligand, three structure types were found in the solid state, *viz*. chelate, cyclic dimer and chain-like coordination polymer. The M^{II} coordination environment is distorted pseudo-tetrahedral in each case. The P–M–N angle is much larger in the chelates (\geq 119°) than in the ligand-bridged structures (\leq 109°). 1 prefers the formation of chelates [$MX_2(1-\kappa^2 N, P)$]. 3 forms coordination equilibria were observed in solution for the molecular complexes obtained with 1 and 2. NMR data indicate that the *N*- and *P*-donor sites interact most strongly with Zn^{II} and Hg^{II}, respectively. While the formation of bis(phosphine)mercury complexes (soft–soft) was easily achieved, no bis(pyridine)zinc complex (borderline–borderline) could be obtained, which is surprising in view of the HSAB principle.

1. Introduction

Pyridylphosphines are highly versatile P,N-ligands which are widely used in coordination chemistry. The combination of a soft P-donor site with a hard N-donor site has been utilised for applications in catalysis and supramolecular chemistry.¹ We have a long-standing interest in ferrocene-based bidentate ligands with a focus on symmetric N,N-ligands which contain a 1,1'ferrocenediyl backbone.² We recently expanded our work to related heteroditopic P,N-systems, since to date the majority of ferrocene-based P,N-ligands do not contain the 1,1'-ferrocenediyl (fc) backbone but rather have the P- and N-donor groups attached to the same cyclopentadienyl ring.³ We have reported already on complexes of the fc-containing pyridyl-amidophosphine ligands $[Fe(C_5H_4-PPh_2){C_5H_4-C(O)NH-(CH_2)_n-2-py}]$ (n = 1, 2; 2-py = pyrid-2-yl) and $[Fe(C_5H_4-PPh_2)\{C_5H_4-C(O)NH-CH_2-4-py\}]$ (4py = pyrid-4-yl),⁴ and the homologous pyridylphosphine ligands $[Fe(C_5H_4-PPh_2)(C_5H_4-2-py)]$ (1) and $[Fe(C_5H_4-PPh_2)(C_5H_4-CH_2-$ 2-py)] (2) (Fig. 1).⁵ We have extended our study of 1 and 2 systematically from the square-planar tetracoordinate Pd^{II} to the



Fig. 1 Heterobidentate ligands investigated in this work.

divalent Group 12 metal centres Zn^{II}, Cd^{II} and Hg^{II}, which prefer an approximately tetrahedral environment in their tetracoordinate state. We have included the pyrid-3-yl (3-py) analogue of 1 in our investigation, viz. [Fe(C₅H₄-PPh₂)(C₅H₄-3-py)] (3) (Fig. 1). The main focus of the present study is the coordination mode of the bidentate ligands 1-3. In previous work, 1 was found to act as a cischelating ligand towards tetracoordinate square-planar Rh^I, Ir^I,⁶ and Pd^{II.5} The homologous ligand 2, which is more flexible due to the presence of the methylene linker between the pyridyl group and the ferrocene moiety, behaves similarly, forming complexes such as, for example, cis-[PdCl₂($2-\kappa^2 N, P$)].⁵ Both ligands exhibit bite angles close to 90° in these square-planar complexes, with the exception of $[Pd(L^{NC})(1-\kappa^2 N, P)]$ (L^{NC} = [(2-dimethylamino- κN)methyl]phenyl- κC^1), which has a bite angle value of 99.13(8)°. The chelate ring sizes are comparatively large, viz. seven atoms in the case of 1 and even eight atoms in the case of 2, so that a nonchelating binding mode is increasingly likely for these ligands.⁷ Note that for the bis(phosphine) ligands Ph₂P-(CH₂)_n-PPh₂ the tendency for chelation is largest for $n = 2.^{8}$ For example, the square-planar complexes [RhCl(CO){Ph₂P-(CH₂)_n-PPh₂- $\kappa^2 P, P'$ }] are *trans*-configurated bis(phosphine)-bridged dimers when n = 1,

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[†] Dedicated to Prof. Dr Hansgeorg Schnöckel on the occasion of his 70th birthday.

[‡] Electronic supplementary information (ESI) available: Figures showing the structures of the crystallographically characterised compounds. CCDC reference numbers 805316–805336. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01810d

3 or 4; a mononuclear *cis*-chelate is observed only in the case of $n = 2.^{9}$ A recent comprehensive study of *P*,*P*- and *P*,*N*-ligands, which utilised the ZnCl₂ and PdCl₂ fragment, respectively, for analysing the chelating interaction for pseudo-tetrahedral and square-planar structures revealed that a fairly limited bite angle range is possible in the case of the latter (mean value 93.5°), whereas with ZnCl₂ the ligands are free to adopt a wide range of bite angles, with no clustering around the ideal tetrahedral angle of 109.5°.¹⁰

2. Results and discussion

Before addressing the coordination behaviour of ligands 1-3, it is useful to provide a survey of closely related complexes for comparison and reference purposes. Only very few examples of structurally characterised Group 12 metal complexes are available which simultaneously contain a phosphine-type P-donor and an amine- or pyridine-type N-donor coordinated to the metal centre. All of them are chelates with ring sizes of five or six atoms. P,N-Coordinated Group 12 metal complexes of the type $[MX_2(PPh_3)Py]$ (Py = pyridine) are unknown. Table 1 contains pertinent bond lengths and angles of structurally characterised complexes of the type $[MX_2(Py)_2]$, $[MX_2(PPh_3)_2]$ and $[MX_2(dppf)]$ (dppf = 1,1'-bis(diphenylphosphino) ferrocene, M = Zn, Cd, Hg;X = Cl, Br, I), together with data of the few known relevant *P*,*N*chelates.11-31 Most of these complexes are four-coordinate and exhibit a distorted pseudo-tetrahedral structure. There are just five exceptions, viz. the chlorido-bridged dimeric P,N-chelates $[CdCl(\mu-Cl){2-py-CH(PPh_2)_2}]_2$ and $[CdCl(\mu-Cl){Et_2N-(CH_2)_2-}]_2$ PPh₂}]₂, whose metal atoms are in a pentacoordinate distorted trigonal-bipyramidal environment and the polymeric chloridobridged bis(pyridine) complexes trans- $[Cd(\mu-Cl)_2(Py)_2]_n$ and trans- $[Hg(\mu-Cl)_2(Py)_2]_n$ as well as their bromido-bridged analogue *trans*- $[Cd(\mu-Br)_2(Py)_2]_n$, whose metal atoms are in a hexacoordinate pseudo-octahedral environment. In the dominant tetracoordinate case, the metal atom is surrounded by two 'normal' (*i.e.* covalent) electron bond pairs (NBPs) and two accepted bond pairs (ABPs) due to the dative $M \leftarrow L$ interactions according to the bond description provided by Haaland,³² who pointed out that (i) dative $M \leftarrow L$ bonds are very sensitive to the environment of the acceptor atom and (ii) the spatial requirements for the bond pairs are in the order NBP > ABP. This explains why interhalide angles X-M-X larger than the ideal tetrahedral angle of 109.5° are commonly observed. Coordination angles in chelate complexes are influenced by the size and flexibility of the chelate ring. A comparison of the unchelated bis(phosphine) complexes $[MX_2(PPh_3)_2]$ with their dppf analogues reveals no substantial coordination angle differences. This indicates only small effects of the formally six-membered chelate ring present in these dppf complexes. By far the smallest coordination angles among the tetracoordinate complexes collected in Table 1 are the P,N-chelate bite angles, which lie in the range of only ca. $77^{\circ}-83^{\circ}$. The average bond lengths for the tetracoordinate cases are the following: Zn–N 2.06 Å, Cd– N 2.27 Å, Hg–N 2.46; Zn–P 2.47 Å, Cd–P 2.64 Å, Hg–P 2.52 Å; Zn-Cl 2.22 Å, Cd-Cl 2.47 Å, Hg-Cl 2.50 Å; Zn-Br 2.35 Å, Cd-Br 2.56 Å, Hg–Br 2.56 Å; Zn–I 2.55 Å, Cd–I 2.72 Å, Hg–I 2.73 Å. The following bond length trends are apparent: M-N Zn < Cd < Hg, M–P Zn \leq Hg < Cd, M–X Zn < Cd \leq Hg. Only the M– P bond length trend is compatible with naïve expectations based solely on the covalent radii of the group 12 metals, viz. Zn <

Hg < Cd. The smaller than expected radius of Hg and higher than expected electronegativity (absolute values: χ_{Zn} 4.45 eV, χ_{Cd} 4.33 eV, χ_{Hg} 4.91 eV)³³ may be rationalised by a combination of lanthanide contraction and relativistic effects.34 While the covalent bond lengths of the linear molecules MX_2 (M = Zn, Cd, Hg; X = Cl, Br, I) nicely follow the trend expected from the covalent radii (Table 2),³⁵ this is not quite the case for the M-X bond lengths in the complexes under consideration here, since the Hg-X bonds are not shorter on average than the corresponding Cd-X bonds. This trend is much more pronounced for the M-N bond lengths, where Hg-N is always considerably longer than Cd-N. An inspection of the interhalide angles X-M-X reveals that this angle is by far largest for the mercury complexes [HgBr₂(Py)₂] and [HgI₂(Py)₂] (>140°), which exhibit particularly long M–N bonds. The smallest interhalide angles (<111°) are observed for the corresponding mercury phosphine complexes, which have short Hg-P bond lengths, slightly shorter even than the average Zn-P bond length of $[ZnCl_2(PPh_3)_2]$. We note in this context that the coordination angles of [HgI₂(PPh₃)₂] are very close to the tetrahedral value of 109.5°, since triphenylphosphine and iodide bind equally strongly to Hg^{II}.³⁶ Considering Haaland's NBP > ABP rule (vide supra), these structural features indicate a comparatively weak dative Hg \leftarrow N interaction and a comparatively strong Hg \leftarrow P interaction of a more covalent nature, in line with Pearson's HSAB principle.³⁷ The fact that dative $M \leftarrow L$ bonds are very sensitive to the environment of the acceptor atom is reflected by the rather different bond angles observed for the monoclinic and orthorhombic form of $[HgCl_2(PPh_3)_2]$ (Table 1), caused by weak secondary interactions commonly summarised as crystal packing forces.³⁸ It is instructive to inspect the values of different bond type radii in this context (Table 3).³⁹⁻⁴² Not surprisingly, the use of effective ionic radii does not lead to a satisfactory agreement with experimentally determined bond lengths. The best agreement, in particular for the M-L bond lengths, is achieved when using Pauling's tetrahedral covalent radii, which reflect a convolution of covalent and dative bonding.32

Complexes with $[Fe(C_5H_4-PPh_2)(C_5H_4-2-py)]$ (1)

We previously reported an improved synthesis of ligand 1⁵ and have now also determined its crystal structure, which exhibits no unexpected features and will therefore not be described here any further (see ESI[±]). The reaction of ligand 1 with one equivalent of metal halide MX₂ (M = Zn, Cd, Hg; X = Cl, Br, I) afforded products of the expected general composition $[MX_2(1)]$. In order to elucidate their solid state structures, single-crystal X-ray diffraction studies were performed for these compounds, with the exception of $[ZnI_2(1)]$, $[CdCl_2(1)]$ and $[HgCl_2(1)]$, for which suitable single crystals could not be obtained, despite many attempts. Instead, single-crystals of the bis(phosphine) complexes $[CdCl_2(1-\kappa P)_2]$ and $[HgCl_2(1-\kappa P)_2]$ were serendipitously isolated in such crystallisation experiments, when utilising a diffusion method (layering a solution of 1 with a solution of the respective metal dichloride). $[HgBr_2(1-\kappa P)_2]$ was intentionally prepared in this context for reference purposes by reacting HgBr₂ with 2 equivalents of ligand 1. Analogous reactions of the other Group 12 metal dibromides with 2 equivalents of ligand 1 did not afford similar bis(phosphine) complexes. Instead, $[MBr_2(1)]$ (M = Zn, Cd) and unreacted 1 were isolated. The results of the structural

Table 1 Pertinent bond lengths (Å) and angles (°) for $[MX_2(Py)_2]$, $[MX_2(PPh_3)_2]$, $[MX_2(dppf)]$ and relevant *P*,*N*-chelates (M = Zn, Cd, Hg; X = Cl, Br, I).I). Mean bond lengths are given in italics for the structures with metal coordination number (CN) 4

	$M-L^a$	M–X	$L-M-L^a$	X–M–X	Ref.
[ZnCl ₂ (Py) ₂]	2.046(5)	2.215(2)	106.3(2)	120.9(1)	11
	2.052(6)	2.228(2)			
	Zn–N 2.05	Zn–Cl 2.22			
$[ZnBr_2(Py)_2]$	2.036(6)	2.354(1)	107.2(2)	120.90(5)	12
	2.043(6)	2.366(1)			
	Zn-N 2.04	Zn–Br 2.36	100.0(4)	100 20(0)	13
$[Znl_2(Py)_2]$	2.05(1)	2.551(2)	109.2(4)	120.32(8)	15
	2.06(1)	2.553(2)			
$[\mathbf{Z}_{\mathbf{n}}\mathbf{C}]$ (DDb)]	2 100 (2)	2n-12.55	114 88(0)	115 1(1)	14
	2.498(3)	2.214(3)	114.88(9)	115.1(1)	
	2.011(5) Zn P 2 55	$Z_{n} = C_{1} + C_{2} + C_{2}$			
$[7_{n}\mathbf{Cl} (\mathbf{NP1})]$	$\mathbf{P} \cdot 2 \cdot \mathbf{305(2)}$	211-C12.22 2 218(2)	82 0(1)	116 53(6)	15
NP1: 8-Ph.P-quinoline	N: 2.104(5)	2.210(2)	02.0(1)	110.55(0)	
ru 1. 6-1 h ₂ 1 -quinonne	14. 2.104(3)	7n-C1 2 21			
[ZnBr ₂ (NP1)]	P· 2 395(1)	2 3601(8)	82 4(1)	115 17(3)	15
NP1: 8-Ph ₂ P-quinoline	$N^{\circ} 2.096(5)$	2,3377(6)	02.1(1)	115.17(5)	
ru r. o r n ₂ r quinonne	11. 2.090(0)	$Z_{n-Br} 2.35$			
[ZnL ₂ (NP1)]	P: 2.390(1)	2.5388(6)	83.30(9)	119.92(2)	15
NP1: 8-Ph ₂ P-quinoline	N: 2.094(3)	2.5509(6)			
$[CdCl_2(Pv)_2]_{b}^{b}$	2.346(2)	2.6487(6)	180	$87.68(2)^{\circ}$	16
		2.6520(6)		$92.32(2)^{c}$	
$[CdBr_2(Pv)_2]_{\mu}^{b}$	2.321(5)	2.7657(7)	180	89.80(3)°	16
2 2 3 2 3 1				90.20(3) ^c	
$[CdI_2(Py)_2]$	2.267(6)	2.6833(10)	95.0(2)	129.37(3)	16
	2.281(6)	2.6901(11)			
	Cd–N 2.27	Cd–I 2.69			
$[CdCl_2(PPh_3)_2]$	2.632(6)	2.440(6)	107.6(2)	113.9(2)	17
	2.635(5)	2.504(6)			
	Cd–P 2.63	CdCl 2.47			
$[CdI_2(PPh_3)_2]$	2.631(2)	2.724(2)	105.1(1)	116.2(1)	18
	2.653(2)	2.731(2)			
	Cd–P 2.64	Cd–I 2.73			
[CdBr ₂ (dppf)]	2.618(2)	2.5553(9)	104.01(5)	110.95(3)	19
	2.655(2)	2.5578(9)			
	Cd–P 2.64	Cd–Br 2.56			
[CdI ₂ (dppf)]	2.633(1)	2.7325(4)	103.67(3)	113.61(1)	20
	2.654(1)	2.7458(4)			
	Cd–P 2.64	Cd–I 2.74			
$[CdCl_2(NP2)]^{\prime}$	P: 2.5925(11)	2.4099(10)	73.30(7)	112.02(4)	21
NP2: 2-py-CH(PPh_2) ₂	N: 2.442(3)	2.5372(11)		99.43(4)	
		2.6515(11)		84.73(4)	22
$[CdCl_2(NP3)]'$	P: 2.5634(12)	2.4277(12)	77.56(9)	112.46(4)	22
NP3: Et_2N -(CH_2) ₂ - PPh_2	N: 2.503(4)	2.4835(11)		94.91(4)	
	2 2666	2.7788(12)	100	85.31(4)	22
$[\operatorname{HgCI}_2(\operatorname{Py})_2]_n^{\nu}$	2.266(6)	2.754(2)	180	90.21(6)	25
$[\mathbf{U}_{-}\mathbf{D}_{-}, (\mathbf{D}_{-})]$	2 28(2)	2.765(2)	00.7(7)	89.79(6)	23
$[\mathbf{HgBr}_2(\mathbf{Py})_2]$	2.38(2)	2.478(3)	90.7(7)	141.2(1)	25
	2.39(2)	2.465(3)			
$[\mathbf{H}_{\mathbf{a}}\mathbf{I}_{\mathbf{b}}(\mathbf{D}_{\mathbf{v}})]$	ng - n 2.39	пg-ы 2.40 2.668(1)	02.8(4)	142.7(1)	24
$[\Pi g I_2(\Gamma y)_2]$	2.424(9)	2.008(1) 2.664(1)	93.8(4)	142.7(1)	
	11g-1N 2.42	2.004(1)			
[HgCl. (PPh.).]	2 503(6)	2 491(7)	113 5(1)	106 6(2)	25 <i>d</i>
	2.532(4)	2.491(7) 2 504(4)	115.5(1)	100.0(2)	
	$H_{\sigma} = P_{2} 52$	H_{g} C1 2 50			
	2.462(2)	2,545(3)	$134\ 1(1)$	110 7(1)	26 <i>e</i>
	2.478(2)	2.559(2)		(-)	
	Hg-P 2.47	Hg-Cl 2.55			
$[HgBr_2(PPh_3)_2]$	2.491(5)	2.627(2)	113.01(14)	107.12(8)	27
	2.550(4)	2.6368(14)			
	Hg–P 2.52	Hg-Br 2.63			
$[HgI_2(PPh_3)_2]$	2.557(3)	2.733(1)	108.95(9)	110.43(4)	28
	2.574(3)	2.763(1)	× /	~ /	
	Hg–P 2.57	Hg–I 2.75			
[HgCl ₂ (dppf)]	2.510(2)	2.510(2)	114.04(5)	105.78(6)	29
	2.5162(16)	2.528(2)			
	Hg–P 2.51	Hg-Cl 2.52			

Table 1 (Contd.)

	M–L ^a	M–X	L-M-L ^a	X–M–X	Ref.
[HgI ₂ (dppf)]	2.5585(15) 2.5718(14) Hg–P 2.57	2.7723(5) 2.7801(5) Hg–I 2.78	106.50(5)	107.119(16)	30
[HgCl ₂ (NP3)] NP3: Et ₂ N-(CH ₂) ₂ -PPh ₂	P: 2.417(3) N: 2.641(11)	2.443(3) 2.445(3) Hg–Cl 2.44	77.7(3)	109.0(1)	31

^a L = ligating atom (N or P). ^b CN 6. ^c cis Cl–M–Cl angle. ^d monoclinic (P2₁/c). ^e orthorhombic (Pna2₁). ^f CN 5.

Table 2 Comparison of bond lengths (Å) for linear MX_2 molecules in the gas phase

	Cl	$\Delta d_{ m Cl/Br}$	Br	$\Delta d_{ m Br/I}$	Ι	Mean Δd
$ Zn \Delta d_{Zn/Cd} Cd \Delta d_{Cd/Hg} Hg Mean \Delta d$	2.064(5) 0.202 2.266(6) -0.026 2.240(7)	0.130 0.120 0.134 <i>0.128</i>	2.194(9) 0.192 2.386(5) -0.012 2.374(12)	0.195 0.184 0.184 <i>0.188</i>	2.389(6) 0.181 2.570(6) -0.012 2.558(7)	0.192 -0.017

Table 3 Survey of relevant covalent and ionic radii

	Covalent radius ^a / ^b	Tetrahedral covalent radius ^e	Effective ionic radius ^d
Zn	1.22/1.18	1.31	0.60 ^e
Cd	1.44/1.36	1.48	0.78^{e}
Hg	1.32/1.33	1.48	0.96 ^e
Cl	1.02/0.99	0.99	1.81
Br	1.20/1.14	1.11	1.96
I	1.39/1.33	1.28	2.20
Ν	0.71/0.71	0.70	
Р	1.07/1.11	1.10	

investigations revealed the P,N-chelate nature of $[MX_2(1)]$ in all but one case. The molecular structure of $[CdBr_2(1)]$ is shown in Fig. 2 as a representative example for the chelates obtained. The structural exception is $[HgI_2(1)]$, which turned out to be the iodidobridged dimer $[HgI(\mu-I)(1-\kappa P)]_2$, which contains ligand 1 in a P-coordinated form (Fig. 3). Pertinent bond lengths and angles are collected for the chelates in Table 4; data for the structurally characterised bis(phosphine) complexes are also included. The bond length trends are essentially identical to those observed for the tetracoordinate complexes collected in Table 1 (M-N Zn < Cd < Hg, M–P Zn \leq Hg < Cd, M–X Zn < Cd \leq Hg; *vide supra*). The chelate ring of $[MX_2(1)]$ contains seven atoms. The bite angle of ligand 1 in these compounds lies in the range of ca. $119^{\circ}-125^{\circ}$, which is much larger than the bite angle range of only ca. $77^{\circ}-83^{\circ}$ observed for the P,N-chelates with 'standard' ring sizes of five and six atoms (Table 1). It is also considerably larger than the bite angles exhibited by ligand 1 in the distorted square-planar d⁸configurated complexes described above, where bite angles close to 90° were observed.

The molecular structures of the bis(phosphine) complexes $[CdCl_2(1-\kappa P)_2]$, $[HgCl_2(1-\kappa P)_2]$ and $[HgBr_2(1-\kappa P)_2]$ are very similar to one another. The latter one is exemplarily shown in Fig. 4. In comparison with their bis(triphenylphosphine) and dppf analogues (Table 1), our complexes tend to exhibit larger P–M–P



Fig. 2 Molecular structure of $[CdBr_2(1)]$ in the crystal.

angles (Δ° ca. 10°–15°) and smaller X–M–X angles (Δ° ca. 10°). It is not clear whether this can be ascribed to the larger steric bulk of ligand **1** vs. PPh₃ and dppf. In view of the quite different bond angles observed for the monoclinic and orthorhombic forms of [HgCl₂(PPh₃)₂] (vide supra), it seems likely that crystal packing forces are more important in this context.

All products obtained showed fairly good solubilities in polar organic solvents. Their structure in solution was probed by NMR spectroscopy in CDCl₃. Metal *N*-coordination leads to a diagnostic shift of the ¹H NMR signal due to the α -pyridyl proton H⁶. Likewise, metal *P*-coordination is reflected by a shift of the ³¹P NMR signal due to the PPh₂ substituent of **1**. Pertinent NMR spectroscopic data are collected in Table 5. A substantial low-field shift ≥ 0.4 ppm of the pyridyl H⁶ NMR signal with respect to the corresponding signal of uncoordinated **1** is observed in all cases except [HgBr₂(**1**- κ *P*)₂], which indeed contains a non-coordinated pyridyl group. This shift is most pronounced in the case of the zinc complexes ($\Delta\delta$ *ca.* 1.1 ppm), which agrees well

 $\label{eq:constraint} \textbf{Table 4} \quad \text{Pertinent bond lengths (Å) and angles (°) for chelate and bis(phosphine) complexes of 1}$

	M–N	M–P	M–X	$L^1 - M - L^2$	Х-М-Х
$[ZnCl2(1-\kappa^2 N, P)]$ 2 independent molecules	2.142(4)	2.4442(14)	2.2609(15) 2.2324(16)	120.42(11)"	113.05(6)
	2.135(4)	2.4623(14)	2.2369(14) 2.2627(15)	124.78(11) ^a	117.60(6)
$[ZnBr2(1-\kappa^2 N, P)]$ 2 independent molecules	2.120(3)	2.4278(10)	2.3704(6) 2.4001(6)	120.22(9) ^a	109.66(2)
	2.139(4)	2.4277(10)	2.3757(6) 2.3981(6)	124.90(10) ^a	115.48(2)
$[\mathbf{CdBr}_2(1{\textbf{-}}\kappa^2N, \boldsymbol{P})]$	2.341(4)	2.6188(12)	2.5596(6) 2.5800(6)	118.70(10) ^a	112.58(2)
$[\mathbf{CdI}_2(1{\textbf{-}}\kappa^2N,\boldsymbol{P})]$	2.375(3)	2.5932(11)	2.7326(4) 2.7520(5)	121.60(9) ^a	116.990(15)
$[\mathbf{HgBr}_2(1{\textbf{-}}\kappa^2 N, \boldsymbol{P})]$	2.573(3)	2.4462(9)	2.6291(5) 2.5574(5)	118.87(7) ^a	111.667(16)
$[CdCl_2(1-\kappa P)_2]$		2.580(2)	2.448(2)	122.04(8)	103.63(9)
$[\text{HgCl}_2(1-\kappa P)_2]$		2.4946(6) 2.4949(6)	2.5554(7) 2.5546(7)	123.99(2) ^b	100.04(3)
$[HgBr_2(1-\kappa P)_2]$		2.5029(11) 2.4971(12)	2.6818(6) 2.6775(6)	124.28(4) ^b	100.26(2)

^{*a*} $L^1 = N, L^2 = P.^{b} L^1 = L^2 = P.$



Fig. 3 Molecular structure of $[HgI(\mu-I)(1-\kappa P)]_2$ in the crystal.

with the notion based on the HSAB principle that among the divalent Group 12 metals the strongest interaction with pyridine type donors is exhibited by Zn^{II}, both partners being borderline between hard and soft.^{37a} The shift observed for the ³¹P NMR signal with respect to non-coordinated **1** is very small in the case of the zinc complexes ($\Delta \delta \leq 3.7$ ppm). It is moderately larger for the cadmium complexes ($\Delta \delta \geq 9.7$ ppm) and substantially larger for the mercury complexes, where low-field shifts of up to *ca.* 50 ppm are observed, indicative of a comparatively robust metal-phosphorus bond, which is also reflected by the observation of ¹⁹⁹Hg satellite signals at room temperature. We have observed

^{111,113}Cd satellite signals only in the case of the bromido complex $[CdBr_2(1)]$, which shows the largest low-field shift of the ³¹P NMR signal among the cadmium chelates of **1** and consequently has the strongest Cd–P interaction in this series. The lability of Cd \leftarrow P bonds, indicated by the absence of ^{111,113}Cd satellite signals in the other two cases, is compatible with results reported for a range of complexes of the type $[CdX_2(PR_3)_2]$, which are known to undergo facile phosphine dissociation.¹⁸ Bürgi *et al.* have demonstrated for $[HgX_2(PPh_3)_2]$ that ${}^{1}J({}^{199}Hg,{}^{31}P)$ coupling constants can be expressed as a function of X–Hg–X and P–Hg–P angles.⁴³ Large coupling constants are accompanied by small X–Hg–X and large



Fig. 4 Molecular structure of $[HgBr_2(1-\kappa P)_2]$ in the crystal.

Table 5 NMR spectroscopic data indicative of the coordination of 1

	¹ H NMR signal pyridyl H ⁶ / $\Delta\delta$	³¹ P NMR signal/ $\Delta\delta$
1	8.47	-17.7
$[ZnCl_2(1)]$	9.57/1.10	-14.0/3.7
$[ZnBr_2(1)]$	9.57/1.10	-14.4/3.3
$[ZnI_2(1)]$	9.60/1.13	-19.2/-1.5
$[CdCl_2(1)]$	8.99/0.52	$-8.0^{a}/9.7$
$[CdBr_2(1)]$	9.35/0.88	-3.6/14.1 (1708, 1782) ^b
$[CdI_2(1)]$	9.27/0.80	$-8.0^{a}/9.7$
$[HgCl_2(1)]$	9.36/0.89	32.2/49.9 (7470) ^c
$[HgBr_2(1)]$	9.15/0.68	$28.5/46.2(6359)^{c}$
$[HgI_2(1)]$	8.89/0.42	19.7ª/37.4
$[\text{HgBr}_2(1-\kappa P)_2]$	8.48	14.5/32.2

^{*a*} broad. ^{*b*} $^{1}J(^{111}Cd,^{31}P)$ and $^{1}J(^{113}Cd,^{31}P)$, respectively, in Hz. ^{*c*} $^{1}J(^{199}Hg,^{31}P)$ in Hz.

P–Hg–P angles and also by short Hg–P bond lengths.⁴⁴ They reported ${}^{1}J({}^{199}\text{Hg},{}^{31}\text{P})$ values of 4675 Hz, 4156 Hz and 3074 Hz for [HgCl₂(PPh₃)₂], [HgBr₂(PPh₃)₂] and [HgI₂(PPh₃)₂], respectively,⁴⁵ which are considerably smaller than the values of 7470 Hz and 6359 Hz obtained for the chelates [HgCl₂(1)] and [HgBr₂(1)],

respectively (Table 5). No such ¹⁹⁹Hg satellites were detected in the case of the bis(phosphine) complex $[HgBr_2(1-\kappa P)_2]$. Among the mercury complexes of 1, this compound exhibits the smallest low-field shift of the ³¹P NMR signal. These spectral features indicate phosphine ligand exchange processes which are fast on the NMR time scale.⁴⁶ In the case of [HgI₂(1)], which is not a chelate in the solid state, but exhibits the iodido-bridged dimeric structure $[HgI(\mu-I)(1-\kappa P)]_2$ (see ESI[‡]), a broad ³¹P NMR signal was observed, compatible with dynamic processes close to the coalescence regime. This compound exhibits the smallest coordination-induced low-field shift of the pyridyl H6 NMR signal of only ca. 0.4 ppm, which indicates a highly dynamic equilibrium in solution, containing similar concentrations of P,N-coordinated chelate and isomers without N-coordination. It is likely that these exclusively P-coordinated isomers are $[HgI_2(1-\kappa P)]$ and $[HgI(\mu-I)(1-\kappa P)]_2$, in accord with findings previously reported for the system HgI₂/PR₃.⁴⁷ The broadness of the ³¹P NMR signal suggests that the monomer-dimer equilibrium of these isomers is comparatively slow on the NMR time scale. Concentrationand temperature-dependent NMR studies would be useful for testing this hypothesis, but were not within the scope of our investigation.

Complexes with $[Fe(C_5H_4-PPh_2)(C_5H_4-CH_2-2-py)]$ (2)

We previously reported the synthesis of ligand 2^5 and have now also determined its crystal structure, which exhibits no unexpected features and will therefore not be described here any further (see ESI[‡]). According to our experience gathered in the chemistry of ligand 1, the Group 12 metal dibromides worked best in terms of crystallinity. They were therefore chosen as primary targets for the study of the coordination behaviour of ligand 2, which is more flexible than 1 due to the presence of the methylene spacer. The reaction of ligand 2 with one equivalent of ZnBr₂ in ethanol and subsequent evaporation of the solvent in vacuo afforded a product whose composition was [ZnBr₂(2)] according to elemental analysis. Single-crystals were obtained by recrystallisation from chloroform. They were subjected to an X-ray diffraction study, which revealed the anticipated chelate structure (Fig. 5). In contrast, storage of the combined ethanolic solutions of 2 and ZnBr₂ at room temperature afforded single crystals of the centrosymmetric *P*,*N*-bridged cyclic dimer $[ZnBr_2(\mu-2)]_2$ (Fig. 6). Interestingly, a reactive diffusion experiment utilising a 2:1 molar ratio of 2 and ZnBr₂ also afforded this cyclic dimer instead of the expected $[ZnBr_2(2)_2]$. Pertinent bond parameters are collected in Table 6 for both isomers. There are no significant bond length differences between the two isomers. While the interhalide angles differ only marginally, we note a pronounced difference in the P-Zn-N angle, which is wider by almost 20° in the chelate compound, the value of 122.64(8)° being almost identical to the average bite angle value observed for the two independent molecules of $[\operatorname{ZnBr}_2(1-\kappa^2 N, P)] \text{ (Table 4).}$



Fig. 5 Molecular structure of the chelate $[ZnBr_2(2-\kappa^2 N, P)]$ in the crystal.

The reaction of ligand 2 with $CdBr_2$ in ethanolic solution afforded a precipitate of the composition [CdBr₂(2)] according to elemental analysis. Unfortunately, single crystals could not be obtained either by simple recrystallisation from chloroform or dichloromethane or by liquid-phase diffusion of non-polar solvents into chlorocarbon solutions of the precipitate. After many unsuccessful attempts, single crystals were finally afforded by a reactive diffusion method using two different solvents. A solution of ligand 2 in dichloromethane was layered first with a small amount of pure ethanol and then with an ethanolic solution of CdBr₂. The crystals turned out to be composed of the coordination polymer $[CdBr_2(\mu-2)]_n$ (Fig. 7), instead of the expected chelate or cyclic dimer. The analogous reaction of 2 with CdI₂ in ethanol gave a precipitate, which could be recrystallised from chloroform by liquid-phase diffusion of hexane, affording the chelate $[CdI_2(2 \kappa^2 N, P$]. Selected bond lengths and angles of these two cadmium complexes are also collected in Table 6. The main difference in bond parameters between the chelate $[CdI_2(2-\kappa^2 N, P)]$ and the polymeric $[CdBr_2(\mu-2)]_n$ is the P-Cd-N angle, which is wider by *ca.* 11° in the chelate.

The reaction of ligand 2 with HgBr₂ in ethanolic solution yielded a precipitate of the composition [HgBr₂(2)] according to elemental analysis. Single-crystals were again obtained by a reactive diffusion method, using ethanol as the solvent. The result of the X-ray diffraction analysis proves the chelate structure of the product obtained. Crystals of a completely different product were isolated when the experiment was performed under mixedsolvent conditions, *i.e.* by layering a dichloromethane solution of 2 with a small amount of pure ethanol and then with an ethanolic solution of HgBr2. Despite the 1:1 molar ratio of the two starting materials and identical concentrations of their solutions, this procedure afforded the polymeric complex $[{HgBr(\mu-Br)}_2(\mu-Br)]_2$ **2**)]_{*n*} (Fig. 8), which has a 1:2 ligand-to-metal stoichiometry. The stoichiometrically "inverse" bis(phosphine) complex [HgBr₂(2)₂] was prepared by reacting $HgBr_2$ and 2 in a 1:2 ratio in ethanol. The precipitate was recrystallised from chloroform by liquid-phase diffusion of hexane, which afforded single crystals of the solvate $[HgBr_2(2)_2]$ ·CHCl₃. Table 6 contains pertinent structural data for these three mercury complexes. A comparison of [HgBr₂(1- $\kappa^2 N, P$ and [HgBr₂(**2**- $\kappa^2 N, P$)] reveals essentially identical Hg–P distances of ca. 2.44 Å, but rather different Hg-N distances of 2.573(3) Å and 2.372(7) Å, respectively. The same M-N bond length trend, although less pronounced, is also observed for the pairs $[\text{ZnBr}_2(1-\kappa^2 N, P)]/[\text{ZnBr}_2(2-\kappa^2 N, P)]$ (average value 2.13 Å vs. 2.09 Å) and $[CdI_2(1-\kappa^2 N, P)]/[CdI_2(2-\kappa^2 N, P)]$ (2.38 Å vs. 2.31 Å). Again, the M-P bond lengths differ only marginally in these pairs. A factor contributing to comparatively shorter M-N bond lengths observed with ligand 2 may be that, owing to the presence of an alkyl substituent on the pyridyl unit, its N-donor strength is higher than that of 1, whose corresponding substituent has an sp² hybridised, and thus more electronegative, pivotal atom. The Pauling electronegativities of C(sp³) and C(sp²) are 2.48 and 2.66, respectively.48 The bite angles of 1 and 2 in their chelates lie in the narrow range between $ca. 119^{\circ}$ and 125° , with no systematic differences between the two ligands. Ligand 2 is coordinatively more flexible and less predictable than 1. It gives us the opportunity to compare P,N-chelates with unchelated analogues, viz. chainlike polymeric and cyclic dimeric complexes, whose P-M-N angles turned out to be much more acute than the chelate bite angles.

Table 6Pertinent bond lengths (Å) and angles (°) for complexes of 2

	M–N	M–P	M–X	L^1-M-L^2	X-M-X
$[\mathbf{ZnBr}_2(2{\boldsymbol{\cdot}}\kappa^2N,\boldsymbol{P})]$	2.087(3)	2.4389(9)	2.4040(5) 2.3904(5)	122.64(8) ^a	114.19(2)
$[ZnBr_2(\mu-2)]_2$	2.097(6)	2.455(2)	2.4003(12) 2.3790(12)	100.5(2) ^a	112.31(5)
$[\mathbf{CdBr}_2(\boldsymbol{\mu}\textbf{-2})]_n$	2.323(7)	2.637(2)	2.5578(10) 2.5734(10)	109.13(19) ^{<i>a</i>}	115.36(4)
$[\mathrm{CdI}_2(2{\boldsymbol{\cdot}}\kappa^2N,\boldsymbol{P})]$	2.309(6)	2.607(2)	2.7675(9) 2.7605(8)	120.0(9) ^a	116.74(3)
$[HgBr_2(2-\kappa^2 N, P)]$	2.372(7)	2.443(2)	2.6120(13) 2.6278(10)	123.8(2) ^a	110.31(4)
$[\{HgBr(\mu\text{-}Br)\}_2(\mu\text{-}2)]_n$	2.365(8)	2.419(3)	2.4710(11) 3.1498(14) 2.8647(12) 2.5319(13) 2.6514(12) 2.5999(12)		
$[HgBr_2(2-\kappa P)_2]$		2.510(2) 2.512(2)	2.6615(8) 2.6640(8)	124.01(5) ^b	

^{*a*} $L^1 = N, L^2 = P.^{b} L^1 = L^2 = P.$



Fig. 6 Molecular structure of the cyclic dimer $[ZnBr_2(\mu-2)]_2$ in the crystal.

The complexes obtained with ligand 2 were studied by NMR spectroscopy in CDCl₃ solution in order to gain insight into their structures in solution. Pertinent data are collected in Table 7.

Although the data set here is not as large as in the case of ligand 1, we can identify salient features which indicate coordination equilibria in solution similar to those discussed in detail for the complexes of 1. In analogy to the results obtained with 1, the signal due to the α -pyridyl H⁶ is low-field shifted with respect to uncoordinated 2 in all cases except the bis(phosphine) complex [HgBr₂(2- κP)₂]. Again, this shift is largest for Zn^{II} and smallest

for Hg^{II}. The general trend concerning the coordination-induced shift of the ³¹P NMR signal is also similar to that found for **1**. The ³¹P NMR signal remains essentially unshifted in the case of Zn^{II}, indicating no substantial Zn–P bonding in solution. While broad ³¹P NMR signals were observed for cadmium complexes of **1**, indicative of dynamic processes close to the coalescence point, no ³¹P NMR signal was detected for [CdBr₂(**2**)], which is therefore in the coalescence regime. The strongest M–P interaction occurs in the case of [HgBr₂(**2**)], as is reflected by the largest $\Delta\delta$ value and the observation of metal–phosphorus coupling for this compound.



Fig. 7 Section of the polymeric chain of $[CdBr_2(\mu-2)]_n$ in the crystal.



Fig. 8 Section of the polymeric chain of $[{HgBr(\mu-Br)}_2(\mu-2)]_n$ in the crystal.

Complexes with $[Fe(C_5H_4-PPh_2)(C_5H_4-3-py)]$ (3)

Attempts to prepare ligand **3** by a Negishi cross-coupling reaction⁴⁹ in analogy to **1** failed. The synthesis was achieved by utilising standard Suzuki–Miyaura cross-coupling methodology instead.⁵⁰ 3-Pyridylboroxin⁵¹ was reacted with 1-bromo-1'-(diphenylphosphino)ferrocene⁵² in a 1,4-dioxane–water mixture in the presence of $[Pd(PPh_3)_4]$ (2.5 mol%) and an excess of potassium carbonate. The product was structurally characterised by a single-

crystal X-ray diffraction analysis, which revealed no unusual features. The structure of **3** is therefore not described here any further (see ESI[‡]). Due to the relative orientation of the *P*- and *N*-donor sites in **3**, this ligand was expected to be unsuitable for chelation and consequently prone to the formation of coordination polymers. Indeed, the reactions of **3** with the Group 12 metal dibromides in a 1:1 molar ratio afforded insoluble, and therefore probably polymeric, materials whose composition was [MBr₂(**3**)] according to elemental analysis. In order to obtain crystals of

Fable 7	NMR spectroscop	ic data indicative	e of the coordination	of 2
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	'Η NMR signal pyridyl H ⁶ /Δδ	³¹ P NMR signal/ $\Delta\delta$
2	8.48	-16.2
$[ZnBr_2(2)]$	9.66/1.18	-18.1/-1.9
$[CdBr_2(2)]$	9.45/0.97	n. d. <i>ª</i>
$[CdI_2(2)]$	9.23/0.75	24.3/40.5
$[HgBr_2(2)]$	9.09/0.61	24.4/40.6 (6321) ^b
$[HgBr_2(2-\kappa P)_2]$	8.44	15.4/31.6
" not detected. ^{b 1} $J($ ¹⁹	⁹ Hg, ³¹ P) in Hz.	

Table 8 Pertinent bond lengths (Å) and angles (°) for complexes of 3

	M–N	M–P	M–X	$L^1 - M - L^2$	X-M-X
$[ZnBr_2(\mu-3)]_n$ $[HgBr_2(\mu-3)]_n$	2.077(4) 2.439(3)	2.4628(14) 2.4423(10)	2.3771(7) 2.3823(7) 2.5727(4) 2.5847(4)d	104.22(12) 107.63(9)	119.20(3) 112.81(2)

these products suitable for a single-crystal X-ray diffraction study, reactive diffusion experiments were carried out by layering a solution of **3** in dichloromethane with a small amount of pure dichloromethane and then with an ethanolic solution of MBr₂. This procedure was successful in the case of M = Zn and Hg. Both compounds exhibit the anticipated polymeric chain structure. We surmise an analogous structure for the cadmium compound. A section of the polymeric chain of $[ZnBr_2(\mu-3)]_n$ is displayed in Fig. 9. Pertinent bond parameters for both structurally characterised complexes are collected in Table 8.

A comparison of these data with those of the corresponding chelate complexes of the pyrid-2-yl analogue 1 shows the following trends. The M–N bond lengths are shorter in the coordination polymers of 3. This effect is relatively small for zinc (Zn–N: 2.08 Å*vs.* 2.13 Å (average value) for [ZnBr₂(1)]), but quite substantial for mercury (Hg–N: 2.44 Å vs. 2.57 Å for [HgBr₂(1)]). The M–P bond lengths, on the other hand, are almost identical. The P–Zn–N angle is wider by ca. 15° in the case of the chelates. These data suggest the presence of significant chelate ring strain in the complexes of ligand 1, affecting particularly the M–N bond.

The polymeric nature of the complexes obtained from 3 and MBr₂ prevented their NMR spectroscopic characterisation in solution. The donor solvent DMSO turned out to dissolve the products by depolymerisation. In the ¹H NMR spectrum the signals due to the pyridyl protons H^2 and H^6 were observed essentially unshifted in comparison to those of uncoordinated 3 in each case. The ³¹P NMR spectrum of the solution of the zinc complex in DMSO exhibited two sharp signals, one at -18.9 ppm (free ligand) and a second one of much lower intensity at 25.3 ppm. The cadmium complex showed essentially identical behaviour. A large excess of DMSO certainly leads to the formation of solvento complexes of the type $[MBr_2(DMSO)_n]$ (M = Zn, Cd),⁵³ thus liberating ligand 3. The minor species responsible for the ³¹P NMR signal at 25.3 ppm in both cases might be [MBr₂(3- κP)(DMSO)_{n-1}]. However, this is extremely unlikely, since in the case of the mercury complex, a single, broad ³¹P NMR signal at 19.3 ppm is observed, clearly indicating P-coordination. An analogous, hypothetical, P-coordination should be weaker in the case of Zn and Cd and should therefore lead to a low-field shift of the ³¹P NMR signal much smaller than that observed in the case of Hg, as was noted above in the chemistry of ligand 1 (Table 5). Furthermore, only a single, averaged, signal would be expected for the fast exchange cases Zn^{II} and Cd^{II}. We therefore believe that the signal at 25.3 ppm is rather due to the corresponding *P*-oxide of **3**, which may be formed slowly in solution by oxygen transfer from DMSO. This type of reaction has been thoroughly investigated for Ph₃P and was shown to be catalysed by Lewis acids.⁵⁴ As a final test of our *P*-oxide hypothesis, **3** was reacted with hydrogen peroxide. This afforded the oxidation product 3O, which indeed exhibited a ³¹P NMR signal at 25.3 ppm in DMSO. We note that phosphine oxides are interesting ligands in their own



Fig. 9 Section of the polymeric chain of $[ZnBr_2(\mu-3)]_n$ in the crystal.

right, which can bind both hard $^{\rm 55}$ and borderline-type $^{\rm 56}$ metal centres. $^{\rm 57}$

3. Conclusions

A main aspect of our study is the preferred coordination mode of the heterobidentate ligands 1-3 in complexes formed with Group 12 metal dihalides MX_2 in a 1 : 1 molar ratio. Three structure types were found in the solid state, viz. chelate (A), cyclic dimer (B) and chain-like coordination polymer (C) (Fig. 10). Irrespective of the structure type, the M^{II} coordination environment is best described as distorted pseudo-tetrahedral in each case. The P-M–N angle is considerably larger in the chelates (type A, $\geq 119^{\circ}$) than in the ligand-bridged structures (types B and C, $\leq 109^{\circ}$). The pyrid-2-yl substituted ligand 1 prefers the formation of chelates $[MX_2(1-\kappa^2 N, P)]$, in which the chelate ring comprises seven atoms. The size of an analogous, hypothetical, chelate ring formed by the pyrid-3-yl analogue 3 is eight atoms. However, due to the relative orientation of its P- and N-donor sites, 3 is unsuitable for chelation. It acts as a bridging ligand, forming coordination polymers $[MX_2(\mu-3)]_n$. Ligand 2 is more flexible than 1 and 3, because its pyridyl group is separated from the ferrocene moiety by a methylene group. Consequently, its coordination behaviour is more temperamental. We have observed all three structure types A-C with 2. On top of that, it is possible that different structure types occur with the same MX₂ fragment, depending on the crystallisation conditions. This was demonstrated for the ZnBr₂ fragment (types A and B). With only a handful of examples reported to date, Group 12 metal complexes which contain a phosphine-type P-donor and an amine- or pyridine-type N-donor are surprisingly rare. Our compounds which belong to structure types B and C are the first examples of this class which are not chelates. In the case of the chelates formed by 1 and 2, the experimentally observed bite angles range from ca. 90°5 to 125° for both ligands, which shows that they can adapt to the requirements of rather diverse metal centres.



Fig. 10 Structure types encountered for 1 : 1 complexes of **1–3** with Group 12 metal dihalides.

NMR spectroscopic data reveal the presence of dynamic coordination equilibria in CDCl₃ solution for the molecular compounds obtained with ligands 1 and 2. Coordination-induced signal shifts indicate that the *N*- and *P*-donor sites interact most strongly with Zn^{II} and Hg^{II}, respectively, in accordance with Pearson's HSAB principle. Not surprisingly, therefore, it proved possible to obtain the Hg^{II} bis(phosphine) complexes such as [HgBr₂(1- κ *P*)₂], which was prepared straightforwardly from 1 and HgBr₂ in a 2 : 1 molar ratio. Interestingly, the reaction of ZnBr₂ with two equivalents of 1 did not afford the respective Zn^{II} bis(pyridine) complex, although this, too, should be a perfect match in terms of the HSAB principle. Instead, the *P*,*N*-chelate [ZnBr₂(1- κ ²*N*,*P*)] was obtained, and one equivalent of 1 remained unreacted, which is entropically more favourable than the formation of [ZnBr₂(1- κ *N*)₂]. These observations suggest that the Zn^{II}–P_{phosphine} interaction is stronger than the Hg^{II} - $N_{pyridine}$ interaction, both being borderline-soft combinations.

4. Experimental

General considerations

All preparations involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen by using standard Schlenk techniques or in a conventional argon-filled glove box. Solvents and reagents were appropriately dried and purified by conventional methods and stored under inert gas atmosphere. 3-Pyridylboroxin⁵¹ and 1-bromo-1'-(diphenylphosphino)ferrocene⁵² were prepared according to published procedures. Elemental analyses were carried out by the microanalytical laboratories of the Institute of Thermal Energy Management at the University of Kassel and the Department of Chemistry, Charles University, Prague. NMR spectra were recorded with the following Varian spectrometers: Unity INOVA (500 MHz), VNMR 500 (500 MHz) and Varian 400-MR (400 MHz). $^{\rm 13}{\rm C}$ and $^{\rm 31}{\rm P}$ NMR data were collected by proton-decoupled methods. Chemical shifts (δ) are given in ppm and are referenced to the signals due to the residual protio impurities of the solvents used relative to tetramethylsilane for ¹H and to the respective solvent signal for ¹³C.^{58,59} In the case of ³¹P NMR spectra obtained from samples in CDCl₃, chemical shifts were indirectly referenced to PPh₃ (δ -6.0 ppm, relative to 85% phosphoric acid in D₂O), spectra obtained from samples in DMSO-d₆ were referenced to external 85% phosphoric acid in DMSO-d₆ (δ 0.0 ppm).⁶⁰ Coupling constants are given as absolute values in Hz. Mass spectra were obtained with a Bruker Esquire 3000 spectrometer (ESI) and a quadrupole ion-trap spectrometer (ESI and APCI) Finnigan LCQDECA (ThermoQuest, San José, USA). MALDI mass spectra were obtained with a BiFlex IV spectrometer (Bruker Daltonics, Bremen, Germany) equipped with an N₂ laser (wavelength 337 nm, 3 ns pulse duration). DCTB (2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2enylidene]malononitrile) was used as matrix.

Preparative work

 $[Fe(C_5H_4-PPh_2)(C_5H_4-3-py)]$ (**3**). A solution of 3pyridylboroxin (0.63 g, 2.0 mmol) and K₂CO₃ (2.80 g, 20.0 mmol) in water (10 mL) and solid [Pd(PPh₃)₄] (115 mg, 0.1 mmol, 2.5 mol%) were added sequentially to a solution of 1-bromo-1'-(diphenylphosphino)ferrocene (1.80 g, 4.0 mmol) in 1,4-dioxane (25 mL). The reaction mixture was stirred at 120 °C (bath temperature) for 14 h and was subsequently allowed to cool to room temperature. The organic layer was separated off. Volatile components were evaporated by using a rotary evaporator. The residue was dissolved in dichloromethane (20 mL). The solution was washed with water $(2 \times 20 \text{ mL})$ and the combined washings extracted with dichloromethane (2 \times 10 mL). The combined organic layers were dried with Na₂SO₄ and filtered. Neutral alumina (5.0 g) was added and volatile compounds were removed in vacuo. The adsorbed material was subjected to column chromatography on neutral alumina, eluting first with a 5:1 mixture of petroleum ether (bp 40 °C-60 °C) and diethyl ether to remove non-polar components and subsequently with chloroform, which afforded 3 as an orange oil, which solidified

upon standing. Yield: 0.76 g (43%). Crystals suitable for a single-crystal X-ray diffraction analysis were obtained by slow evaporation of a concentrated dichloromethane solution. ¹H NMR (CDCl₃): δ 3.96 (m, 2H, fc), 4.22 (m, 2H, fc), 4.26 (m, 2H, fc), 4.56 (m, 2H, fc), 7.15 (m, 1H, Py), 7.30-7.36 (m, 10H, Ph), 7.58 (m, 1H, Py), 8.40 (m, 1H, Py), 8.61 (m, 1H, Py). ¹H NMR (DMSO-d₆): δ 3.88 (s, 2H, fc), 4.22 (s, 2H, fc), 4.27 (s, 2H, fc), 4.78 (s, 2H, fc), 7.27 (m, 1H, Py), 7.30-7.37 (m, 10H, Ph), 7.59 (m, 1H, Py), 8.40 (m, 1H, Py), 8.61 (m, 1H, Py). ¹³C{¹H} NMR (CDCl₃): δ 67.67 (d, J_{PC} = 1 Hz), 70.94 (d, J_{PC} = 1 Hz), 73.08 (d, $J_{\rm PC} = 4$ Hz), 74.52 (d, $J_{\rm PC} = 15$ Hz), 82.56, 123.38, 128.33 (d, $J_{\rm PC} =$ 7 Hz), 128.73, 133.37, 133.59 (d, $J_{PC} = 20$ Hz), 134.82, 138.96 (d, $J_{\rm PC} = 10$ Hz), 147.33, 147.56. ³¹P{¹H} NMR (CDCl₃): δ -17.8. ³¹P{¹H} NMR (DMSO-d₆): δ –18.8. MS/APCI(+): m/z (%) 464 $(45) [MO + H]^+, 448 (100) [M + H]^+, 370 (21) [C_{21}H_{17}FeNP]^+, 263$ (15) [C₁₅H₁₂FeN]⁺. Calc. for C₂₇H₂₂NFeP (477.3): C, 72.50; H, 4.96; N, 3.13. Found: C, 73.34; H, 4.94; N, 3.23%.

[Fe(C₅H₄–P(O)Ph₂)(C₅H₄-3-py)] (3O). Hydrogen peroxide (0.01 mL of a 30% aqueous solution, 0.1 mmol) was added to solution of 3 (22.3 mg, 0.05 mmol) in acetone (5 mL). The mixture was stirred for 1 h. Volatile components were removed *in vacuo*. Water (5 mL) was added and the mixture extracted with dichloromethane (3 × 2 mL). The combined extracts were dried with Na₂SO₄ and filtered. The solution was reduced to dryness *in vacuo*, affording 3O as an orange solid in essentially quantitative yield. ¹H NMR (DMSO-d₆): δ 4.17 (s, 2H, fc), 4.22 (s, 2H, fc), 4.40 (s, 2H, fc), 4.86 (s, 2H, fc), 7.32 (m, 1H, Py), 7.51 (m, 4H, Ph), 7.58 (m, 2H, Ph), 7.65 (m, 4H, Ph), 7.85 (m, 1H, Py), 8.52 (m, 1H, Py), 8.81 (m, 1H, Py). ³¹P{¹H} NMR (DMSO-d₆): δ 25.3. MS/ESI(+): *m/z* (%) 463 (100) [C₂₇H₂₂FeNOP]⁺.

General procedure for the preparation of metal complexes

Solid metal halide MX_2 (M = Zn, Cd, Hg and X = Cl, Br, I) (0.1 mmol) was added to a solution of one (0.1 mmol) or two equivalents (0.2 mmol) of the respective ligand in ethanol (10 mL). The mixture was stirred at room temperature for 14 h. If precipitation of the product occurred, the solvent volume was reduced in vacuo to slightly less than half. If no precipitation occurred, the solvent was completely removed in vacuo, the residue was dissolved in dichloromethane and hexane was added carefully to precipitate the product. In either case a suspension of the respective product was obtained. The solid was isolated by filtration, washed with diethyl ether (2 mL) and subsequently with hexane (5 mL) and was finally dried in vacuo. Reactive diffusion experiments to obtain crystalline material directly from the reaction were carried out in a 5 mm NMR tube. Typically, equal volumes (ca. 0.5 mL) of 0.1 M solutions of the respective starting materials were used for the layering experiments. Possible variations are given in the detailed descriptions.

[ZnCl₂(1)]. Reactants: **1** (44.7 mg, 0.1 mmol), ZnCl₂ (13.6 mg, 0.1 mmol). Work-up: The solvent was evaporated *in vacuo* and the residue dissolved in dichloromethane (2 mL). [ZnCl₂(1)] was precipitated with hexane (25 mL). Yield: 55 mg (95%). Crystals suitable for a single-crystal X-ray diffraction analysis were obtained by layering a dichloromethane solution of **1** with a solution of ZnCl₂ in diethyl ether. ¹H NMR (CDCl₃): δ 4.30 (m, 4H, fc), 4.58 (m, 2H, fc), 5.19 (m, 2H, fc), 7.42 (m, 8H, Ph + Py),

7.76 (m, 5H, Ph + Py), 9.57 (m, 1H, Py). ¹³C{¹H} NMR (CDCl₃): δ 71.41, 71.59, 73.39 (d, $J_{PC} = 6$ Hz), 75.63 (d, $J_{PC} = 10$ Hz), 84.34, 123.10, 125.22, 128.98 (d, $J_{PC} = 10$ Hz), 131.22, 133.79 (d, $J_{PC} = 13$ Hz), 139.32, 152.78, 158.46. ³¹P{¹H} NMR (CDCl₃): δ –14.0. MS/ESI(+): m/z (%) 605 (10) [M + Na]⁺, 546 (20) [M - Cl]⁺, 510 (35) [C₂₇H₂₂FeNPZn]⁺, 464 (30) [C₂₇H₂₂FeNPO]⁺, 448 (100) [C₂₇H₂₂FeNP]⁺. Calc. for C₂₇H₂₂NCl₂FePZn (583.6): C, 55.57; H, 3.80; N, 2.40. Found: C, 56.27; H, 3.84; N 2.57%.

[ZnBr₂(1)]. Reactants: 1 (44.7 mg, 0.1 mmol), ZnBr₂ (22.5 mg, 0.1 mmol). Work-up: The solvent was evaporated in vacuo and the residue dissolved in dichloromethane (2 mL). Hexane (15 mL) was added. The solid precipitate was isolated by filtration, washed with hexane (5 mL) and dried in vacuo. This procedure afforded $[ZnBr_2(1)] \cdot \frac{1}{4}C_6H_{14}$. Yield: 41 mg (61%). Single-crystals suitable for an X-ray diffraction analysis were obtained in analogy to the procedure described for [ZnCl₂(1)]. ¹H NMR (CDCl₃): δ 4.23 (m, 2H, fc), 4.54 (m, 2H, fc), 4.60 (m, 2H, fc), 5.02 (m, 2H, fc), 7.43 (m, 8H, Ph + Py), 7.78 (m, 5H, Ph + Py), 9.57 (m, 1H, Py). ¹³C{¹H} NMR (CDCl₃): δ 71.32, 71.40, 73.7 (br d, $J_{PC} \approx 5$ Hz), 75.97 (d, $J_{PC} = 12$ Hz), 84.75, 123.12, 125.10, 128.96 (d, $J_{PC} = 10$ Hz), 131.22, 133.82 (d, $J_{PC} = 12$ Hz), 139.29, 153.46, 157.93 (s). ³¹P{¹H} NMR (CDCl₃): δ –14.4. MS/ESI(+) m/z (%) 592 (15) [M – Br]⁺, 510 (15) [C₂₇H₂₂FeNPZn]⁺, 464 (22) [C₂₇H₂₂FeNPO]⁺, 448 (100) $[C_{27}H_{22}FeNP]^+$. Calc. for $C_{27}H_{22}NBr_2FePZn \cdot \frac{1}{4}C_6H_{14}$ (694.0): C, 49.32; H, 3.70; N, 2.02. Found: C, 49.73; H, 3.73; N 2.16%.

[ZnI₂(1)]. Reactants: 1 (44.7 mg, 0.1 mmol), ZnI₂ (31.9 mg, 0.1 mmol). Work-up: The solvent volume was reduced to slightly more than half and the product precipitated by addition of hexane (10 mL). Yield: 49 mg (65%). ¹H NMR (CDCl₃): δ 4.18 (m, 2H, fc), 4.60 (m, 2H, fc), 4.69 (m, 2H, fc), 4.94 (m, 2H, fc), 7.38 (m, 1H, Py), 7.41–7.52 (m, 7H, Ph + Py), 7.74–7.83 (m, 5H, Ph + Py), 9.60 (m, 1H, Py). ¹³C{¹H} NMR (CDCl₃): δ 70.95, 71.34, 73.79 (d, $J_{PC} = 10$ Hz), 76.14 (d, $J_{PC} = 12$ Hz), 77.36, 84.88, 122.87, 124.67, 128.91 (d, $J_{PC} = 10$ Hz), 130.60 (d, $J_{PC} = 39$ Hz), 131.18, 134.01 (d, $J_{PC} = 11$ Hz), 139.26, 153.95, 157.45. ³¹P{¹H} NMR (CDCl₃): δ –19.2. MS/ESI(+): m/z (%) 767 (7) [M]⁺, 510 (33) [C₂₇H₂₂FeNPZn]⁺, 447 (100) [C₂₇H₂₂FeNP]⁺. Calc. for C₂₇H₂₂NFeI₂PZn (766.5): C, 42.31; H, 2.89; N 1.83. Found: C, 42.29; H, 3.12; N 1.80%.

[CdCl₂(1)]. Reactants: 1 (44.7 mg, 0.1 mmol), CdCl₂ (18.3 mg, 0.1 mmol). Work-up: The product was isolated by filtration directly from the reaction mixture. Yield: 14 mg (22%). ¹H NMR (CDCl₃): δ 4.12 (s, 2H, fc), 4.27 (s, 2H, fc), 4.43 (s, 2H, fc), 5.04 (s, 2H, fc), 7.25 (m, 1H, Py), 7.37 (m, 1H, Py), 7.41 (m, 6H, Ph), 7.59 (m, 4H, Ph), 7.65 (m, 1H, Py), 8.99 (br s, 1H, Py). ¹³C{¹H} NMR (CDCl₃): δ 68.28, 71.56, 73.23 (d, $J_{PC} = 6$ Hz), 75.15 (d, $J_{PC} = 13$ Hz), 77.36, 84.73, 122.82, 128.93, 129.18 (d, $J_{PC} = 10$ Hz), 130.03, 131.22, 133.77 (d, $J_{PC} = 14$ Hz), 138.69, 152.03, 158.26, 167.90. ³¹P{¹H} NMR (CDCl₃): δ -8.0 (br). Calc. for C₂₇H₂₂NCdCl₂FeP (630.6): C, 51.43; H, 3.52; N, 2.22. Found: C, 52.44; H, 3.52; N, 2.33%.

[CdBr₂(1)]. Reactants: **1** (44.7 mg, 0.1 mmol), CdBr₂·4H₂O (34.4 mg, 0.1 mmol). Work-up: The product was isolated by filtration directly from the reaction mixture. Yield: 43 mg (60%). Single-crystals suitable for an X-ray diffraction analysis were obtained by slow evaporation of a dichloromethane solution of the product. ¹H NMR (CDCl₃): δ 4.21 (m, 2H, fc), 4.27 (m, 2H, fc), 4.60 (m, 2H, fc), 5.19 (m, 2H, fc), 7.38 (m, 1H, Py), 7.44–7.52 (m, 7H, Ph + Py), 7.72 (m, 1H, Py), 7.75 (m, 4H, Ph), 9.35 (m, 1H,

Py). ¹³C{¹H} NMR (CDCl₃): δ 71.05, 71.44, 73.44 (d, J_{PC} = 7 Hz), 75.62 (d, J_{PC} = 13 Hz), 77.36, 85.06, 123.19, 124.48, 129.22 (d, J_{PC} = 10 Hz), 129.42, 131.58 (d, J_{PC} = 2 Hz), 133.80 (d, J_{PC} = 13 Hz), 139.12, 152.87, 157.88. ³¹P{¹H} NMR (CDCl₃): δ -3.6 ($J_{111_{CdP}}$ = 1708 Hz, $J_{113_{CdP}}$ = 1782 Hz). MS/MALDI(+): m/z (%) 639 (21) [M - Br]⁺, 446 (100) [C₂₇H₂₂FeNP]⁺. Calc. for C₂₇H₂₂NBr₂CdFeP (719.5): C, 45.07; H, 3.08; N, 1.95. Found: C, 45.32; H, 3.00; N, 2.07%.

[CdI₂(1)]. Reactants: 1 (44.7 mg, 0.1 mmol), CdI₂ (36.6 mg, 0.1 mmol). Work-up: The solvent volume was reduced to slightly more than half in vacuo and hexane (10 mL) was added. The precipitate was isolated by filtration, washed with hexane (5 mL) and dried *in vacuo*. This procedure afforded $[CdI_2(1)] \cdot \frac{1}{2}C_6H_{14}$. Yield: 25 mg (34%). Single-crystals suitable for an X-ray diffraction analysis were obtained by layering a chloroform solution of the product with hexane. ¹H NMR (CDCl₃): δ 4.21 (m, 2H, fc), 4.34 (m, 2H, fc), 4.57 (m, 2H, fc), 5.06 (m, 2H, fc), 7.34–7.40 (m, 2H, Py), 7.43–7.52 (m, 6H, Ph), 7.67–7.74 (m, 5H, Ph + Py), 9.27 (m, 1H, Py). ¹³C{¹H} NMR (CDCl₃): δ 70.66, 71.31, 73.55 (d, J_{PC} = 6 Hz), 75.76 (d, J_{PC} = 12 Hz), 77.40, 85.42, 122.88, 123.94, 129.07 (d, $J_{PC} = 10$ Hz), 131.21 (d, $J_{PC} = 44$ Hz), 131.23, 133.90 (d, $J_{PC} =$ 13 Hz), 134.18, 138.67, 153.08, 157.56. ³¹P{¹H} NMR (CDCl₃): δ -8.9 (br). MS/ESI(+): m/z (%) 838 (3) [M + Na]⁺, 688 (15) [M - I]⁺, 464 (34) [C₂₇H₂₂FeNPO]⁺, 448 (100) [C₂₇H₂₂FeNP]⁺. Calc. for $C_{27}H_{22}NCdFeI_2P \cdot \frac{1}{2}C_6H_{14}$ (856.6): C, 42.07; H, 3.41; N, 1.64. Found: C, 42.63; H, 2.98; N, 1.73%.

[HgCl₂(1)]. Reactants: **1** (44.7 mg, 0.1 mmol), HgCl₂ (27.1 mg, 0.1 mmol). Work-up: The solvent volume was reduced to *ca*. one third *in vacuo*. The precipitate was filtered off, washed and dried *in vacuo*. Yield: 61 mg (84%). ¹H NMR (CDCl₃): δ 4.25 (s, 2H, fc), 4.32 (s, 2H, fc), 4.60 (s, 2H, fc), 5.19 (s, 2H, fc), 7.30 (m, 1H, Py), 7.36 (m, 1H, Py), 7.56 (m, 6H, Ph), 7.64 (m, 1H, Py), 7.80 (m, 4H, Ph), 9.36 (m, 1H, Py). ¹³C{¹H} NMR (CDCl₃): δ 71.44, 71.47, 74.08 (d, $J_{PC} = 9$ Hz), 75.53 (d, $J_{PC} = 14$ Hz), 77.36, 86.36, 122.91, 123.25, 127.75 (d, $J_{PC} = 52$ Hz), 129.70 (d, $J_{PC} = 11$ Hz), 132.69 (d, $J_{PC} = 3$ Hz), 133.61 (d, $J_{PC} = 13$ Hz), 137.72, 152.21, 156.97. ³¹P{¹H} NMR (CDCl₃): δ 32.2 ($J_{199}_{HgP} = 7470$ Hz). MS/ESI(+): *m/z* (%) 684 (100) [M - Cl]⁺, 447 (35) [C₂₇H₂₂FeNP]⁺. Calc. for C₂₇H₂₂NCl₂FeHgP (718.8): C, 45.12; H, 3.08; N 1.95. Found: C, 45.28; H, 3.15; N, 1.94%.

[HgBr₂(1)]. Reactants: 1 (44.7 mg, 0.1 mmol), HgBr₂ (36.0 mg, 0.1 mmol). Work-up: The product was isolated by filtration directly from the reaction mixture. Yield: 67 mg (83%). Single-crystals suitable for an X-ray diffraction analysis were obtained by layering a dichloromethane solution of the product with a small amount of pure dichloromethane and then with diethyl ether. ¹H NMR (CDCl₃): δ 4.33 (m, 2H, fc), 4.38 (m, 2H, fc), 4.57 (m, 2H, fc), 5.11 (m, 2H, fc), 7.24 (m, 1H, Py), 7.30 (m, 1H, Py), 7.52-7.62 (m, 7H, Ph + Py), 7.77 (m, 4H, Ph), 9.15 (m, 1H, Py). ${}^{13}C{}^{1}H{}$ NMR (CDCl₃): δ 70.75, 71.62, 74.47 (d, J_{PC} = 9 Hz), 75.52 (d, J_{PC} = 13 Hz), 86.46, 122.46, 122.54, 129.58 (d, $J_{PC} = 9$ Hz), 132.49 (d, $J_{\rm PC} = 2 \,{\rm Hz}$, 133.64 (d, $J_{\rm PC} = 13 \,{\rm Hz}$), 137.35, 152.04, 156.84. ³¹P{¹H} NMR (CDCl₃): δ 28.5 (J_{199}_{HgP} = 6359 Hz). MS/MALDI(+): m/z (%) 728 (80) [M - Br]⁺, 447 (100) [C₂₇H₂₂FeNP]⁺. Calc. for C₂₇H₂₂NBr₂FeHgP (807.7): C, 40.15; H, 2.75; N, 1.73. Found: C, 40.21; H, 2.58; N, 1.84%.

 $[HgI_2(1)]$. Reactants: 1 (44.7 mg, 0.1 mmol), HgI_2 (45.4 mg, 0.1 mmol). Work-up: Hexane (10 mL) was added to the reaction mixture. The precipitate was isolated by filtration, washed with hexane (5 mL) and dried in vacuo. This procedure afforded $[HgI_2(1)] \cdot \frac{1}{4}C_6H_{14}$. Yield: 72 mg (80%). Single-crystals suitable for an X-ray diffraction analysis were obtained by recrystallisation from chloroform. ¹H NMR (CDCl₃): δ 4.23 (m, 2H, fc), 4.37 (m, 2H, fc), 4.44 (m, 2H, fc), 4.98 (m, 2H, fc), 7.18 (m, 1H, Py), 7.24 (m, 1H, Py), 7.45–7.55 (m, 6H, Ph), 7.57 (m, 1H, Py), 7.66 (m, 4H, Ph), 8.89 (m, 1H, Py). ${}^{13}C{}^{1}H{}$ NMR (CDCl₃): δ 70.03, 70.30, 71.71, 74.44 (d, $J_{PC} = 8$ Hz), 75.43 (d, $J_{PC} = 13$ Hz), 86.39, 121.57, 122.12, 129.5 (d, J_{PC} = 12 Hz), 131.95, 133.68 (d, J_{PC} = 12 Hz), 136.93, 151.72, 156.85. 31P{ 1 H} NMR (CDCl₃): δ 19.74 (br). MS/ESI(+): m/z (%) 776 (33) $[M - I]^+$, 448 (100) $[C_{27}H_{22}FeNP]^+$. Calc. for C₂₇H₂₂NFeHgI₂P·¹/₄C₆H₁₄ (923.2): C, 37.08; H, 2.78; N, 1.52. Found: C, 37.65; H, 2.61; N, 1.62%.

[CdCl₂(1)₂]. The product was obtained by serendipity in a reactive diffusion experiment aimed at producing single-crystals of [CdCl₂(1)] by layering a 0.1 M solution of 1 in dichloromethane with an equal volume (0.5 mL) of a 0.1 M solution of CdCl₂ in diethyl ether.

[HgCl₂(1)₂]. The product was obtained by serendipity in a reactive diffusion experiment aimed at producing single-crystals of $[HgCl_2(1)]$ by layering a 0.1 M solution of 1 in dichloromethane with an equal volume (0.5 mL) of a 0.1 M solution of $HgCl_2$ in diethyl ether.

 $[HgBr_2(1)_2]$. Reactants: 1 (89.4 mg, 0.2 mmol), $HgBr_2$ (36.0 mg, 0.1 mmol). Work-up: The product was isolated by filtration directly from the reaction mixture. The solid was washed with ethanol (5 mL) and dried in vacuo. Yield: 107 mg (85%). Single-crystals suitable for an X-ray diffraction analysis were obtained by layering a dichloromethane solution of the product with a small amount of pure dichloromethane and then with diethyl ether. ¹H NMR (CDCl₃): δ 4.12 (m, 4H, fc), 4.19 (m, 4H, fc), 4.36 (m, 4H, fc), 4.86 (m, 4H, fc), 7.05 (m, 2H, Py), 7.15 (m, 2H, Py), 7.36 (m, 8H, Ph + Py), 7.43-7.51 (m, 8H, Ph), 7.35-7.45 (m, 6H, Ph + Py), 7.61 (m, 8H, Ph), 8.48 (m, 2H, Py). $^{13}C{^{1}H} NMR (CDCl_3): \delta 69.19, 70.42, 72.94, 74.76, 77.39, 85.41,$ 120.85, 121.13, 128.99, 131.27, 133.71, 136.29, 149.55, 157.74. ³¹P{¹H} NMR (CDCl₃): δ 14.5. MS/ESI(+): m/z (%) 1254 (3) $[M]^+$, 1175 (4) $[M - Br]^+$, 728 (19) $[C_{27}H_{22}FeNPHgBr]^+$, 448 (100) [C₂₇H₂₂FeNP]⁺. Calc. for C₅₄H₄₄N₂Br₂Fe₂HgP₂ (1254.9): C, 51.68; H, 3.53; N, 2.23. Found: C, 51.32; H, 3.49; N, 2.05%.

[ZnBr₂(2)]. Reactants: **2** (23.1 mg, 0.05 mmol), ZnBr₂ (11.3 mg, 0.05 mmol). Procedure: The starting materials were each dissolved in ethanol (5 mL) and the solutions combined. The mixture was stirred for 30 min. Volatile components were removed in *vacuo*. The residue was dissolved in dichloromethane (1 mL) and the solution added dropwise to hexane (10 mL). The precipitate was filtered off, washed with hexane (5 mL) and dried *in vacuo*. This procedure afforded [ZnBr₂(**2**)] $\cdot \frac{1}{4}$ CH₂Cl₂. Yield: 30 mg (90%). Single-crystals suitable for an X-ray diffraction analysis were obtained by liquid-phase diffusion of hexane into a chloroform solution of the product. ¹H NMR (CDCl₃): δ 3.85 (br s, 2H), 4.01 (s, 2H), 4.37–4.59 (br m, 6H), (Fc + CH₂Py); 7.39 (m, 5H, Ph + Py), 7.45 (m, 2H, Ph), 7.52 (m, 1H, Py), 7.55–7.82 (br m, 4H, Ph), 7.96 (m, 1H, Py), 9.66 (m, 1H, Py). ¹³C{¹H} NMR (CDCl₃):

 T_{\min}/T_{\max} T/K

a/Å b/Å

c/Å

 α (°) β (°)

γ(°

Ζ

 $R_{\rm int}$ Refl. obsd

V/Å

 $D_{\rm c}/{\rm g}~{\rm cm}^{-1}$ $\mu/{\rm mm}^{-1}$

Refl. measured

 R_1 , w R_2 ($I > 2\sigma(I)$)

 R_1 , w R_2 (all data)

 $\Delta \rho_{\rm min}/_{\rm max}//{\rm e}~{\rm \AA}^{-3}$

Unique refl.

Crystal system

Space group

View Article Online

δ 37.45, 68.96, 69.83, 72.92, 74.24, 77.36, 87.01, 123.58, 127.19, 128.85 (d, $J_{PC} = 10$ Hz), 130.16 (d, $J_{PC} = 40$ Hz), 131.06, 133.91 (d, $J_{PC} = 12$ Hz), 140.56, 150.96, 159.96. ³¹P{¹H} NMR (CDCl₃): δ –18.1. MS/ESI(+): m/z (%) 524 (100) [C₂₈H₂₄FeNPZn]⁺. Calc. for C₂₈H₂₄NBr₂FeZnP· $\frac{1}{4}$ CH₂Cl₂ (707.7): C, 47.94; H, 3.49; N, 1.98. Found: C, 47.59; H, 3.58; N 1.92%.

[ZnBr₂(\mu-2)]₂]. Reactants: 2 (46.1 mg, 0.1 mmol), ZnBr₂ (22.5 mg, 0.1 mmol). Work-up: The volume of the solution was reduced to *ca*. one half *in vacuo*. The solution was stored for 3 d at room temperature, which afforded crystals suitable for a single-crystal X-ray diffraction analysis. Yield: 42 mg (61%).

[CdBr₂(2)]. Reactants: **2** (23.1 mg, 0.05 mmol), CdBr₂·4H₂O (17.2 mg, 0.05 mmol). Procedure: The starting materials were each dissolved in ethanol (10 mL) and the solutions combined. The mixture was stirred for 1 h. The precipitate was isolated by filtration, washed and dried *in vacuo*. Yield: 34 mg (94%). ¹H NMR (CDCl₃): δ 3.96, 4.00, 4.29, 4.48, 4.52 (5 s, 5 × 2H, fc + CH₂), 7.35 (m, 1H, Py), 7.39–7.53 (m, 7H, Ph + Py), 7.62 (m, 4H, Ph), 7.92 (m, 1H, Py), 9.45 (m, 1H, Py). ¹³C{¹H} NMR (CDCl₃): δ 38.35, 68.64, 70.31, 72.93 (d, $J_{PC} = 7$ Hz), 74.51 (d, $J_{PC} = 12$ Hz), 77.39, 87.12, 123.61, 126.38, 129.16 (d, $J_{PC} = 10$ Hz), 131.33, 133.71 (d, $J_{PC} = 14$ Hz), 140.26, 150.77, 160.50. ³¹P{¹H} NMR (CDCl₃): No signal could be detected. Calc. for C₂₈H₂₄NBr₂CdFeP (733.5): C, 45.85; H, 3.30; N, 1.91. Found: C, 45.68; H, 3.27; N, 1.85%.

 $[CdBr_2(\mu-2)]_n$. Single-crystals were obtained by layering a 0.1 M solution of 2 in dichloromethane (0.5 mL) with a small amount of pure ethanol and then with a 0.1 M solution (0.5 mL) of $CdBr_2 \cdot 4H_2O$ in ethanol.

[CdI₂(2)]. Reactants: **2** (46.1 mg, 0.1 mmol), CdI₂ (0.1 mmol, 36.6 mg). The procedure was analogous to that described for [CdBr₂(**2**)]. Yield: 37.3 mg (90%). Single-crystals suitable for an X-ray diffraction analysis were obtained by liquid-phase diffusion of hexane into a chloroform solution of the product. ¹H NMR

Table 9 Crystal data and structure refinement details for ligands 1-3

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 $\begin{array}{l} ({\rm CDCl}_3): \ \delta \ 4.04, \ 4.07, \ 4.17, \ 4.39, \ 4.55 \ (5 \ {\rm s}, \ 5 \times 2{\rm H}, \ {\rm fc} + {\rm CH}_2), \\ 7.22 \ ({\rm m}, \ 1{\rm H}, \ {\rm Py}), \ 7.35 \ ({\rm m}, \ 1{\rm H}, \ {\rm Py}), \ 7.50 \ ({\rm m}, \ 6{\rm H}, \ {\rm Ph}), \ 7.73 \ ({\rm m}, \ 5{\rm H}, \ {\rm P} + {\rm Py}), \ 9.23 \ ({\rm m}, \ 1{\rm H}, \ {\rm Py}), \ ^{13}{\rm C}\{^1{\rm H}\} \ {\rm NMR} \ ({\rm CDCl}_3): \ \delta \ 37.63, \\ 69.25, \ 70.64, \ 73.69 \ ({\rm d}, \ J_{\rm PC} = 8 \ {\rm Hz}), \ 74.65 \ ({\rm d}, \ J_{\rm PC} = 12 \ {\rm Hz}), \ 77.39, \\ 88.49, \ 122.90, \ 125.11, \ 129.48 \ ({\rm d}, \ J_{\rm PC} = 12 \ {\rm Hz}), \ 132.27, \ 133.56 \ ({\rm d}, \ J_{\rm PC} = 13 \ {\rm Hz}), \ 138.45, \ 150.16, \ 159.88. \ ^{31}{\rm P}\{^1{\rm H}\} \ {\rm NMR} \ ({\rm CDCl}_3): \ \delta \ 24.3. \ {\rm Calc. \ for \ C_{28}H_{24}{\rm NCdFeI_2P} \ (827.5): \ {\rm C}, \ 40.64; \ {\rm H}, \ 2.92; \ {\rm N}, \ 1.69. \\ {\rm Found: \ C, \ 40.40; \ {\rm H}, \ 2.93; \ {\rm N} \ 1.68\%. \end{array}$

[HgBr₂(2)]. Reactants: 2 (23.1 mg, 0.05 mmol), HgBr₂ (18.0 mg, 0.05 mmol). Procedure: The starting materials were each dissolved in ethanol (10 mL) and the solutions combined. The mixture was stirred for 1 h. The precipitate was isolated by filtration, washed and dried in vacuo. Yield: 37 mg (91%). Singlecrystals suitable for an X-ray diffraction analysis were obtained by layering a 0.1 M solution of HgBr₂ in ethanol (0.1 mL) with a 0.1 M solution of the 2 in ethanol (0.1 mL). ¹H NMR (CDCl₃): δ 4.07, 4.10, 4.12, 4.55 (4 s, $4H + 3 \times 2H$, fc + CH₂), 7.19 (m, 1H, Py), 7.30 (m, 1H, Py), 7.51 (m, 6H, Ph), 7.69–7.72 (m, 5H, Ph + Py), 9.09 (m, 1H, Py). ¹³C{¹H} NMR (CDCl₃): δ 37.65, 69.84, 70.69, 73.84 (d, $J_{PC} = 9$ Hz), 74.61 (d, $J_{PC} = 13$ Hz), 77.39, 88.38, 122.73, 124.82, 128.83 (d, $J_{PC} = 51$ Hz), 129.50 (d, $J_{PC} = 12$ Hz), 132.31 (d, $J_{PC} = 3$ Hz), 133.55 (d, $J_{PC} = 13$ Hz), 138.29, 149.93, 159.92. ³¹P{¹H} NMR (CDCl₃): δ 24.4 (J_{199}_{HgP} = 6321 Hz). MS/ESI(+): m/z (%) 742 (76) [C₂₈H₂₄BrFeHgNP]⁺, 462 (100) [C₂₈H₂₄FeNP]⁺. Calc. for C₂₈H₂₄Br₂FeHgNP (821.7): C, 40.93; H, 2.94; N, 1.71. Found: C, 40.93; H, 2.94; N, 1.69%.

 $[{HgBr(\mu-Br)}_2(\mu-2)]_n$. Single-crystals were obtained from HgBr₂ and 2 in analogy to the procedure described for $[CdBr_2(\mu-2)]_n$.

[HgBr₂(2)₂]. Reactants: 2 (92.3 mg, 0.2 mmol), HgBr₂ (36.0 mg 0.1 mmol). Work-up: Immediately after the addition of the metal salt a yellow solid precipitated. The reaction mixture was stirred for 14 h, the precipitate was filtered off, washed with ethanol

3

C27H22FeNP

 $0.25 \times 0.21 \times 0.02$

447.28

173(2)

ΡĪ

Triclinic

10.1847(12)

11.0585(12)

10.9491(13)

72.890(9)

85.100(10)

65.974(8)

1075.6(2)

1.381

0.789

7001

3555

2598

0.0534

0.0483, 0.1119

0.0677, 0.1182

-0.584/0.550

0.55/0.56

2

C28H24FeNP

 $0.57 \times 0.40 \times 0.15$

461.30

100(2)

ΡĪ

Triclinic

8.4956(11)

10.9419(13)

13.4071(15)

67.813(9)

75.752(9)

84.294(10)

1118.5(2)

1.370

0.761

8622

3867

3663

0.0501

0.0323, 0.0892

0.0336, 0.0900

-0.445/0.383

0.72/0.88

Dalton Trans., 2011, 40 , 4722–4740	4735

		-
Empirical formula	$C_{27}H_{22}$ FeNP	
Molecular weight	447.28	
Crystal size/mm	$0.49 \times 0.39 \times 0.24$	

1

0.72/0.82

173(2)

ΡĪ

Triclinic

10.1437(9)

11.0401(9)

10.9432(9)

72.013(6)

85.964(7)

66.324(6)

1.394

0.797

9178

3636

3430

0.0340

0.0264, 0.0732

0.0278, 0.0739

-0.357/0.311

1065.47(16)

 Table 10
 Crystal data and structure refinement details for complexes of ligand 1

	$[\operatorname{ZnCl}_2^-, (1^{-\kappa^2}N, P)]$	$[\operatorname{ZnBr}_2^-, (1 \text{-} \kappa^2 N, P)]$	$[CdBr_2 - (1-\kappa^2 N, P)]$	$[\operatorname{Cdl}_2(1\text{-}\kappa^2N,P)]$	$[\operatorname{HgBr}_{2}\text{-}$ (1- $\kappa^{2}N, P$)]	[CdCl ₂ (1- <i>kP</i>)]	$[\mathrm{HgCl}_2(1\text{-}\kappa P)_2]$	$[\mathrm{HgBr}_2(1\text{-}\kappa P)_2]$	[HgI(μ-I)(1- κP)] ₂ .2CHCl ₃
Empirical formula	$\mathrm{C}_{27}\mathrm{H}_{22}\mathrm{Cl}_2$ - FeNPZn	$C_{27}H_{22}Br_{2}$ - FeNPZn	$C_{27}H_{22}Br_{2}$ - CdFeNP	$C_{27}H_{22}CdFeI_2-$ NP	C ₂₇ H ₂₂ Br ₂ - FeHgNP	C ₅₄ H ₄₄ CdCl ₂ - Fe,N,P,	C ₅₄ H ₄₄ Cl ₂ Fe ₂ - HgN,P,	C ₅₄ H ₄₄ Br ₂ Fe ₂ - HgN,P,	${ m C}_{56}{ m H}_{46}{ m Cl}_{6}{ m Fe}_{2}-{ m Hg}_{14}{ m N},{ m P}_{2}$
Molecular weight	583.55	672.47	719.50	813.48	807.69	1077.85	1166.04	1254.96	2042.07
Crystal size/mm	$0.37 \times 0.10 \times 0.03$	$0.33 \times 0.23 \times 0.16$	$0.32\times0.20\times0.02$	$0.36 \times 0.19 \times 0.04$	$0.18 \times 0.16 \times 0.05$	$0.43 \times 0.04 \times 0.03$	$0.60 \times 0.46 \times 0.13$	$0.42\times0.28\times0.17$	$0.11 \times 0.11 \times 0.01$
$T_{\rm min}/T_{\rm max}$	0.75/0.94	0.34/0.47	0.33/0.91	0.27/0.85	0.22/0.60	0.62/0.97	0.07/0.39	0.32/0.72	0.45/0.92
T/\mathbf{K}	203(2)	173(2)	203(2)	193(2)	100(2)	173(2)	203(2)	173(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$P 2_1/c$	$P 2_1$	$P 2_1/c$	$P\overline{1}$	$P\overline{1}$	F dd2	$P 2_1/n$	$P 2_1/n$	$P\bar{1}$
a/Å	19.2868(16)	14.6245(6)	14.8184(13)	10.4638(10)	10.1471(10)	49.456(5)	17.1944(5)	17.4068(8)	9.5405(11)
$b/ m \AA$	9.2179(5)	9.2633(4)	9.3495(6)	10.5429(8)	10.3258(10)	22.4070(14)	15.4843(5)	15.5806(5)	9.8309(13)
$c/\text{\AA}$	28.835(3)	19.3704(7)	18.8737(17)	14.1699(11)	13.6179(13)	8.2534(7)	17.6894(5)	17.5380(8)	16.591(2)
α (°)	90	90	90	72.904(6)	104.921(8)	90	90	90	79.405(11)
β (°)	101.856(7)	102.744(3)	91.972(7)	69.694(7)	92.316(8)	90	92.045(2)	92.161(4)	86.852(10)
χ (°)	90	90	90	70.125(7)	110.214(8)	90	90	90	89.624(10)
$V/Å^3$	5017.1(7)	2559.49(18)	2613.3(4)	1351.0(2)	1280.6(2)	9146.0(13)	4706.7(2)	4753.1(3)	1527.2(3)
Ζ	8	4	4	2	2	8	4	4	1
$D_{ m c}/{ m g~cm^{-1}}$	1.545	1.745	1.829	2.000	2.095	1.566	1.646	1.754	2.220
μ/mm^{-1}	1.827	4.705	4.504	3.684	9.752	1.314	4.083	5.612	7.851
Refl. measured	31242	16734	16395	8799	9514	14627	63890	30291	10365
Unique refl.	8832	4708	4593	4481	4485	3764	8920	8305	5303
$R_{ m int}$	0.0847	0.0473	0.0789	0.0464	0.0411	0.0896	0.0814	0.0776	0.0879
Refl. obsd	5152	4513	3022	3978	4156	2968	7954	7436	3609
$R_1, WR_2 (I > 2\sigma(I))$	0.0461, 0.0876	0.0184, 0.0457	0.0310, 0.0605	0.0282, 0.0758	0.0224, 0.0529	0.0408, 0.0759	0.0276, 0.0702	0.0474, 0.1142	0.0538, 0.1220
R_1 , w R_2 (all data)	0.0890, 0.0948	0.0198, 0.0461	0.0549, 0.0638	0.0324, 0.0835	0.0249, 0.0536	0.0568, 0.0797	0.0318, 0.0720	0.0513, 0.1165	0.0832, 0.1345
$\Delta ho_{ m min}/_{ m max}$ / / e Å $^{-3}$	-0.612/0.901	-0.433/0.339	-0.448/0.730	-0.845/0.793	-1.305/1.628	-0.950/0.470	-2.387/0.864	-2.843/4.258	-1.866/1.149

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abla 11 – Crucetal data and structure refinement dataile for comulavae of livend 2

Iable 11 Crystal data s	und structure refinement d	letails for complexes of light	gand Z				
	$[\operatorname{Zn}\operatorname{Br}_2$ - $(2$ - $\operatorname{K}^2N,P)]$	$[\mathbf{ZnBr}_2(\boldsymbol{\mu}-2)]_2\cdot \mathbf{2CH}_2\mathbf{CI}_2$	[CdBr ₂ - (μ-2)] _n	$[\operatorname{CdI}_2(2\text{-}\kappa^2N,P)]$	$[\operatorname{HgBr}_{2^{2}} - (2^{2}\kappa^{2}N, P)]$	$[\{HgBr(\mu-Br)\}_2-(\mu-2)]_n$	$[HgBr_2(2-\kappa P)_2]\cdot CHCl_3$
Empirical formula	C ₂₈ H ₂₄ - Br: FeNDZn	C ₃₈ H ₅₂ Br ₄ Cl ₄ - Fe.N.P.7n.	C38H24Br2- CdFeNP	C ₂₈ H ₂₄ CdFeI ₂ - NP	С ₂₈ Н ₂₄ Вг2- БеН 0NP	C ₂₈ H ₂₄ Br ₄ FeHg ₂ - NP	C ₅₇ H ₄₉ Br ₂ Cl ₃ Fe ₂ - H σN2P.
Molecular weight	686.49	1542.84	733.52	827.50	821.71	1182.12	1402.38
Crystal size/mm	$0.60 \times 0.09 \times 0.04$	$0.24\times0.20\times0.05$	$0.32 \times 0.20 \times 0.05$	$0.27 \times 0.05 \times 0.05$	$0.39 \times 0.04 \times 0.04$	$0.49 \times 0.17 \times 0.14$	$0.31 \times 0.20 \times 0.15$
$T_{ m min}/T_{ m max}$	0.28/0.79	0.52/0.82	0.27/0.63	0.52/0.85	0.35/0.73	0.01/0.17	0.42/0.58
T/K	218(2)	173(2)	173(2)	100(2)	218(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P 2_1/n$	$P 2_1/n$	$P\overline{1}$	$P 2_1/n$	$P 2_1/n$	P ccn	I ba2
a/Å	9.2769(5)	12.0066(9)	9.1388(11)	9.4757(8)	9.3132(8)	34.9720(12)	13.7805(6)
$b/\text{\AA}$	18.5543(9)	14.5539(7)	9.5318(10)	19.0085(11)	18.5685(17)	9.9410(5)	40.4138(16)
$c/ m \AA$	15.1266(8)	18.3142(14)	16.6270(17)	15.4717(12)	15.3200(13)	18.1638(8)	19.1500(9)
α (°)	90	90	84.260(9)	90	90	90	06
β (°)	93.655(4)	108.865(6)	74.946(9)	94.513(6)	94.473(7)	90	06
γ (°)	90	90	77.441(9)	90	90	90	06
$V/Å^3$	2598.4(2)	3028.4(4)	1363.7(3)	2778.1(4)	2641.3(4)	6314.8(5)	10665.1(8)
Z	4	0	5	4	4	8	8
$D_{ m c}/{ m g~cm^{-1}}$	1.755	1.692	1.786	1.978	2.066	2.487	1.747
μ/mm^{-1}	4.636	4.159	4.317	3.585	9.459	15.286	5.158
Refl. measured	14373	19330	8927	14403	11523	37537	33209
Unique refl.	4562	5342	4563	4897	4552	5554	9405
$R_{ m int}$	0.0445	0.1594	0.1210	0.1141	0.0746	0.0981	0.0850
Refl. obsd	3659	3458	3667	3388	2932	4561	8569
$R_1, \operatorname{w} R_2 \left(I > 2\sigma(I) \right)$	0.0296, 0.0685	0.0663, 0.1610	0.0773, 0.1969	0.0460, 0.1027	0.0334, 0.0841	0.0548, 0.1360	0.0382, 0.0963
R_1 , w R_2 (all data)	0.0419, 0.0714	0.0983, 0.1777	0.0877, 0.2059	0.0726, 0.1101	0.0669, 0.0901	0.0681, 0.1469	0.0430, 0.1010
$\Delta ho_{ m min}/_{ m max}//{ m e}~{ m \AA}^{-3}$	-0.646/0.999	-0.889/1.307	-1.885/3.222	-0.915/0.765	-1.043/1.067	-2.254/4.385	-1.340/2.009

(10 mL) and diethyl ether (20 mL) and dried *in vacuo*. Yield: 71.1 mg (55%). Single-crystals suitable for an X-ray diffraction analysis were obtained by layering a chloroform solution of the product with hexane. ¹H NMR (CDCl₃): δ 3.48 (s, 4H, CH₂), 3.92 (s, 4H, fc), 4.06 (s, 4H, fc), 4.19 (s, 4H, fc), 4.30 (s, 4H, fc), 7.04 (m, 4H, Py), 7.36(m, 8H, Ph), 7.44 (m, 4H, Ph), 7.51 (m, 2H, Py), 7.66 (m, 8H, Ph), 8.44 (s, 2H, Py). ¹³C{¹H} NMR (CDCl₃): δ 37.98, 70.53, 70.99, 73.31, 74.44, 77.36, 88.12, 121.34, 122.99, 128.93, 131.23, 133.75, 136.67, 148.92, 160.79. ³¹P{¹H} NMR (CDCl₃): δ 15.4. MS/APCI(+): *m/z* (%) 1283 (3) [M]⁺, 1202 (5) [M – Br]⁺, 741 (46) [C₂₈H₂₄BrFeHgNP]⁺, 462 (100) [C₂₈H₂₄FeNP]⁺. Calc. for C₅₆H₄₈N₂Br₂Fe₂HgP₂ (1283.0): C, 52.42; H, 3.77; N, 2.18. Found: C, 52.68; H, 3.25; N 2.19%.

[ZnBr₂(µ-3)]_n. Reactants: 3 (44.7 mg, 0.1 mmol), ZnBr₂ (22.5 mg, 0.1 mmol). Work-up: Immediately after the addition of the metal salt a yellow solid precipitated. The reaction mixture was stirred for 6 h. The solvent volume was reduced to ca. one half in vacuo. The solid was filtered off, washed with ethanol (5 mL) and dried in vacuo. Yield: 42 mg (53%). Crystals suitable for an X-ray diffraction analysis were obtained by layering a 0.1 M dichloromethane solution of 3(0.5 mL) with a small amount pure ethanol and then with a 0.1 M solution of ZnBr₂ (0.5 mL). ¹H NMR (DMSO-d₆): δ 3.88 (s, 2H, fc), 4.22 (s, 2H, fc), 4.28 (s, 2H, fc), 4.77 (s, 2H, fc), 7.31 (m, 5H, Ph + Py), 7.34 (m, 6H, Ph), 7.79 (m, 1H, Py), 8.38 (m, 1H, Py), 8.67 (m, 1H, Py). ¹³C{¹H} NMR (DMSO-d₆): δ 67.52, 70.55, 72.83 (d, J_{PC} = 4 Hz), 74.02 (d, J_{PC} = 15 Hz), 76.42 (d, J_{PC} = 8 Hz), 81.98, 123.62, 128.34 (d, J_{PC} = 7 Hz), 128.68, 133.04 (d, J_{PC} = 20 Hz), 133.41, 134.40, 138.53 (d, J_{PC} = 10 Hz), 146.78, 146.87. ³¹P{¹H} NMR (DMSO-d₆): δ –18.9, 25.3. MS/MALDI(+): m/z (%) 447 (100) [C₂₇H₂₂FeNP]⁺.

[CdBr₂(μ-3)]_{*n*}. Reactants: **3** (44.7 mg, 0.1 mmol), CdBr₂·4H₂O (34.4 mg, 0.1 mmol). Work-up: Immediately after the addition of the metal salt a yellow solid precipitated. The reaction mixture was stirred for 14 h. The solid was filtered off, washed with ethanol (5 mL) and dried *in vacuo*. Yield: 30 mg (38%). ¹H NMR (DMSO-d₆): δ 3.89 (s, 2H, fc), 4.22 (s, 2H, fc), 4.28 (s, 2H, fc), 4.77 (s, 2H, fc), 7.29 (m, 5H, Ph + Py), 7.34 (m, 6H, Ph), 7.78 (m, 1H, Py), 8.38 (m, 1H, Py), 8.67 (s, 1H, Py). ¹³C{¹H} NMR (DMSO-d₆): δ 67.46, 70.51, 72.80 (d, J_{PC} = 4 Hz), 73.98 (d, J_{PC} = 15 Hz), 76.38 (d, J_{PC} = 8 Hz), 82.03, 123.49, 128.31 (d, J_{PC} = 7 Hz), 128.65, 132.92, 133.18 (d, J_{PC} = 20 Hz), 134.25, 138.49, 146.89, 146.94. ³¹P{¹H} NMR (DMSO-d₆): δ -18.8, 25.3. MS/MALDI(+): *m/z* (%) 447 (100) [C₂₇H₂₂FeNP]⁺. Calc. for C₂₇H₂₂NBr₂CdFeP (719.5): C, 45.07; H, 3.08; N, 1.95. Found: C, 44.77; H, 3.02; N 1.88%.

[HgBr₂(µ-3)]_{*n*}. Reactants: **3** (44.7 mg, 0.1 mmol) and HgBr₂ (36.0 mg, 0.1 mmol). Work-up: Immediately after the addition of the metal salt a light orange solid precipitated. The reaction mixture was stirred for 14 h. The solid was filtered off, washed with ethanol (5 mL) and dried *in vacuo*. Yield: 55 mg (68%). Single-crystals suitable for an X-ray diffraction analysis were obtained by layering a 0.1 M dichloromethane solution of **3** (0.5 mL) with a small amount pure dichloromethane and then with a 0.1 M solution of HgBr₂ in ethanol (0.5 mL). ¹H NMR (DMSO-d₆): δ 4.41–4.46 (m, 6H, fc), 4.85 (s, 2H, fc), 7.53 (m, 5H, Ph + Py), 7.61 (m, 7H, Ph + Py), 8.36 (m, 1H, Py), 8.57 (m, 1H, Py). ¹³C{¹H} NMR (DMSO-d₆): δ 68.11, 71.56, 73.55 (d, $J_{PC} = 13$ Hz), 74.65 (d, $J_{PC} = 7$ Hz), 83.48, 123.53, 129.35 (d, $J_{PC} = 11$ Hz), 130.76 (d, $J_{PC} = 2$

Table 12Crystal data and structure refinement details for complexes ofligand 3

	$[ZnBr_2(\mu-3)]_n$	$[HgBr_2(\mu-3)]_n$
Empirical formula Molecular weight Crystal size/mm T_{min}/T_{max} T/K Crystal system Space group a/Å b/Å c/Å a (°) β (°) γ (°) $V/Å^3$ Z $D_c/g cm^{-1}$ u/mm^{-1} Refl. measured Unique refl. R_{int} Refl. obsd	$[ZnBr_{2}(\mu-3)]_{n}$ $C_{27}H_{22}Br_{2}FeNPZn$ 672.47 0.13 × 0.12 × 0.09 0.55/0.67 100(2) Monoclinic P 2_{1}/c 15.3284(10) 9.0578(6) 18.4976(10) 90 96.220(5) 90 2553.1(3) 4 1.749 4.716 16069 4461 0.0776 3378	$[HgBr_{2}(\mu-3)]_{n}$ $C_{27}H_{22}Br_{2}FeHgNP$ 807.69 0.60 × 0.45 × 0.09 0.05/0.39 173(2) Monoclinic P 2 ₁ /c 16.0531(9) 8.9781(4) 19.1000(11) 90 105.934(4) 90 2647.0(2) 4 2.027 9.436 16588 4720 0.0518 4423
$R_1, wR_2 (I > 2\sigma(I))$ $R_1, wR_2 (all data)$ $\Delta \rho_{\min} / \max / e Å^{-3}$	0.0408, 0.0861 0.0595, 0.0915 -0.747/2.014	0.0261, 0.0723 0.0285, 0.0734 -0.731/0.933

10 Hz), 132.28, 133.01 (d, $J_{PC} = 13$ Hz), 133.15, 146.85, 147.37. ³¹P{¹H} NMR (DMSO-d₆): δ 19.3 (br). MS/MALDI(+): m/z(%) 808 (8) [C₂₇H₂₂Br₂FeHgNP]⁺, 728 (29) [C₂₇H₂₂BrFeHgNP]⁺, 447 (100) [C₂₇H₂₂FeNP]⁺. Calc. for C₂₇H₂₂NBr₂FeHgP (807.7): C, 40.15; H, 2.75; N, 1.73. Found: C, 40.15; H, 2.72; N 1.79%.

Crystal structure analyses

For each data collection a single-crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. Data collection using Mo-K α radiation ($\lambda = 0.71073$ Å) was made on a Stoe IPDS2 diffractometer equipped with a 2circle goniometer and an area detector. Absorption correction was done by integration using X-red.⁶¹ The data sets were corrected for Lorentz and polarisation effects. The structures were solved by direct methods (SHELXS97) and refined using alternating cycles of least squares refinements against F^2 (SHELXL97).⁶² All non-H atoms were found in difference Fourier maps and were refined with anisotropic displacement parameters. A solvent molecule (probably ethanol) in $[{HgBr(\mu-Br)}_2(\mu-2)]_n$ was not included to the model using the SQUEEZE routine in PLATON.63 H atoms were placed in constrained positions according to the riding model with the 1.2 fold isotropic displacement parameters. Crystallographic details are collected in Tables 9–12. Graphical representations were made using ORTEP-3 win.⁶⁴ All figures represent the displacement ellipsoids at the 30% probability level, except for the H atoms, which are drawn as circles of arbitrary radius.

Acknowledgements

This work was supported by the Czech Science Foundation (project no. P207/10/0176) and a bilateral KONTAKT program by the Ministry of Education of the Czech Republic (project

MEB100906) and the Deutscher Akademischer Austauschdienst (project D/07/01319).

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