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Clathrochelates meet phosphorus: thiophosphorylation of Fe(II) dichloroclathrochelate precursor, synthesis of N,S-donor macrobicyclic ligands and their Pd(II) complexes as potent catalysts of Suzuki cross-coupling reaction†‡§¶

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Nucleophilic substitution of an iron(II) dichloroclathrochelate with diphenylphosphine sulfide under PTC afforded a monophosphorylated cage complex. This precursor undergoes further nucleophilic substitution with mono- and diamines giving *P,N*-substituted mono- and bis-clathrochelates; those with thiophosphoryl and pyridyl groups were used as N,S-donor macrobicyclic ligands toward the palladium(II) ion. In the resulting Pd,Fe-binuclear 1 : 1 complexes, the clathrochelate moieties retain the geometry, characteristic of low-spin iron(II) complexes, with a minor distortion caused by intramolecular interactions. The Pd^{2+} ion has a twisted square-planar N_2SCl-environment. The complexes thus obtained proved to be efficient catalysts of the Suzuki cross-coupling reaction.

Introduction

During the last decade, functionalized cage metal complexes (clathrochelates[1]) and the hybrid nanosized molecular and supramolecular systems based on them have been intensively studied as prospective molecular electronic devices[2] and sensors,[3] very efficient electrocatalysts for hydrogen production,[4] electrochromic materials[5], potent targeting compounds for the ^{10}B-NCT treatment of tumor diseases[6] and transcription inhibitors for various enzymes (T7 RNA and DNA polymerases,[7] and HIV protease[8]). The latter, for instance, make them prospective antiviral and antitumor drug candidates (so-called "topological drugs"[9]).

Ribbed functionalizing substituents in their chelate α-dioximate fragments affect spatial and electronic structures of the clathrochelate framework and, as a result, chemical reactivity of the caging ligands and redox properties of an encapsulated metal ion. N,O,S,C-Nucleophilic substitution of the pre-synthesized reactive mono- and polyhalogenoclathrochelate precursors is reported to be the most convenient and easiest pathway for such functionalization;[10] it has been widely used for the design of different types of ribbed-functionalized clathrochelates and their derivatives. Cage metal complexes with inherent phosphorus-containing pendant substituents, however, have not been reported to date, mostly due to synthetic challenges (see the Results and discussion part). At the same time, such (thio)phosphorylated cage complexes seem to be prospective precursors for the design of hybrid and multicentered systems with unusual chemical, redox and catalytic properties.

Clathrochelates with donor (thio)phosphoryl groups are of special interest, as such groups can be used to synthesize various polynuclear systems for practical applications. In particular, complexes of rare earth metals, scandium(III), copper, palladium, platinum, zinc and nickel(II) ions with phosphorus-containing ligands have been used for their selective extraction

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† Dedicated to the memory of our colleague Prof. I. L. Odinets who passed away on 26 June, 2012.

‡ This title was inspired by a title of the lecture of Prof. E. Hey-Hawkins "Carbaborane meets phosphorus", EUROBORON-6, Radziejowice, Poland, 8–13th September 2013.

§ A preliminary account of this work was presented at the 19th International Conference on Phosphorus Chemistry, Rotterdam, 8–12 July, 2012. (I. L. Odinets, O. I. Artyushin, E. V. Matveeva, A. V. Vologzhanina and Y. Z. Voloshin, *Phosphorus, Sulfur, Silicon*, 2013, **188**, 159–161.)

¶ Electronic supplementary information (ESI) available: Crystallographic and UV-vis tables. CCDC 973317–973323. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53590h

and separation[11] as well as luminescent materials.[12] The palladium(II) complexes of functionalized phosphine ligands are also efficient metallocomplex catalysts of the homogenous Suzuki and Heck coupling reactions,[13] *e.g.* of aryl halides with phenylboronic acids[14]. These cross-coupling reactions are among the most powerful methods for C_{Ar}–C_{Ar} bond formation, owing to the commercial availability of such aryl halides, their tolerance for a broad range of functionalities, as well as the easy handling of the non-toxic boron-containing by-products. They are very useful on an industrial level, mainly for the synthesis of pharmaceuticals and fine chemicals. The use of cage complexes with redox active encapsulated metallocenters as the donor "building blocks" (*i.e.* as clathrochelate ligands) in this case allows the production of electrochemically operated metallocomplex catalytic systems for homogenous reactions of this type.

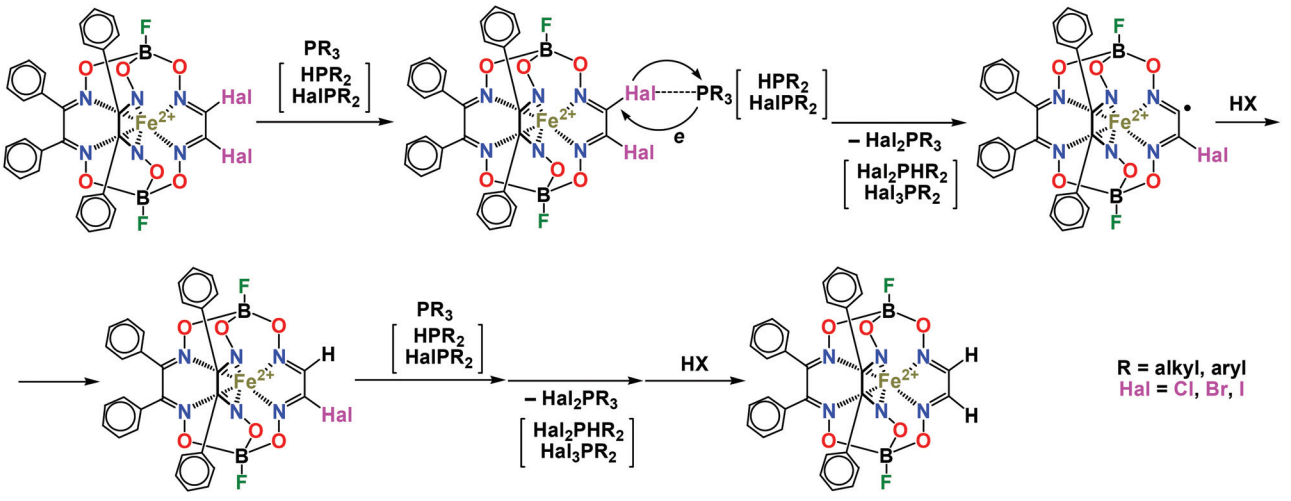
In this paper, we describe the synthesis and X-ray structures of the first phosphorylated clathrochelate, its reactivity in nucleophilic substitution reactions, coordination-chemical properties of mixed *P,N*-substituted ribbed-functionalized cage compounds as macrobicyclic N,S-donor ligands toward palladium(II) ion and a catalytic activity of the Pd,Fe-binuclear complexes obtained in the Suzuki cross-coupling reaction.

Results and discussion

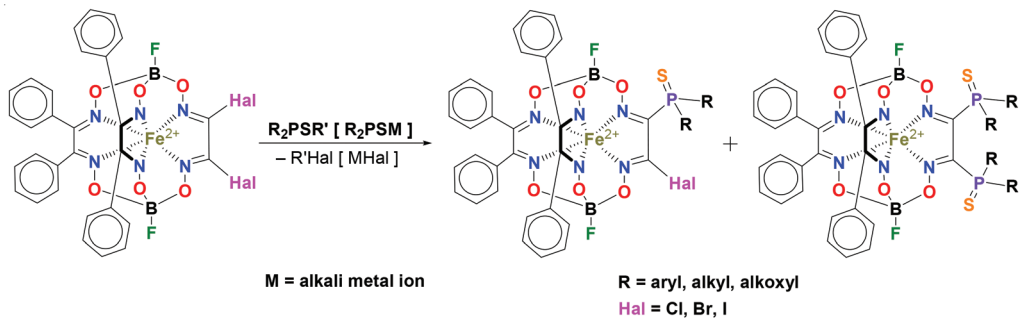
The reactions of the dichloroclathrochelate precursor $FeBd_2(Cl_2Gm)(BF)_2$ (where Bd^{2-} and Gm^{2-} are α-benzyldioxime and glyoxime dianions, respectively) with organophosphorus(III) compounds (di- and trialkyl(aryl)phosphines and their halogen-containing derivatives) did not give the target phosphine cage complexes, but mainly resulted in the side reduction–hydrodehalogenation processes (Scheme 1), affording mono- and dimethine clathrochelate by-products. The same reduction–hydrodehalogenation reactions (but with copper(I) ion as a reductant) have been earlier described for the diiodoclathrochelate precursor $FeBd_2(I_2Gm)(BF)_2$.[10i] The plausible mechanism of this reaction includes the formation of clathrochelate anion radicals by a reduction of the precursor with a corresponding phosphine and an abstraction of a hydrogen atom from a solvent or reactants by these very reactive species (Scheme 1).

As a result, we chose the nucleophilic substitution with organophosphorus(V) derivatives for the synthesis of phosphorus-containing iron(II) clathrochelates. The most feasible pathway to mono- and difunctionalized thio- and phosphorylated iron(II) clathrochelates is based on the stepwise nucleophilic substitution of their dihalogenoclathrochelate precursors, with the corresponding phosphorus-containing nucleophiles (Scheme 2). The same reactions with O,N,S,-C-nucleophiles have been intensively used for the synthesis of a wide range of monoribbed-functionalized iron and cobalt(II) clathrochelates. We, however, failed to perform such a phosphorylation under the typical conditions of the Arbuzov and Michaelis–Becker reactions (inert solvent and temperature range 0–150 °C), as a result of the decomposition of the clathrochelate framework dominating under these reaction conditions.

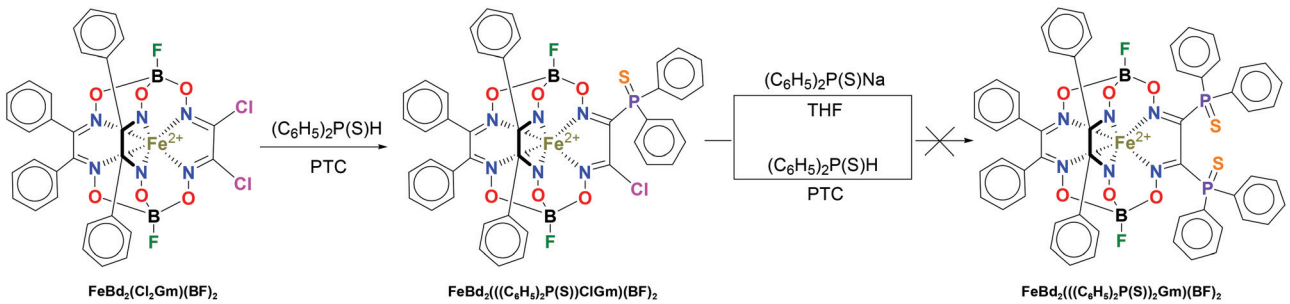
As it has been shown earlier,[15] switching to phase-transfer conditions (PTC) is a good choice if the use of the above reaction conditions gives no phosphorylated products. Indeed, nucleophilic substitution of dichloroclathrochelate precursor $FeBd_2(Cl_2Gm)(BF)_2$ with diphenylphosphine sulfide in Scheme 3 under PTC resulted in the formation of monochloromonothiophosphorylated cage complex $FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$ in high yield even at a 5-fold excess of the thiophosphorylating agent. This thiophosphorylated iron(II) monochloroclathrochelate undergoes no further thiophosphorylation, leading to the dithiophosphorylated complex even under the typical phosphorylation reaction conditions (Scheme 3); however, these attempts led to the complete destruction of its clathrochelate framework. This fact may be explained by steric hindrances between the two bulky diphe-



Scheme 1 The plausible mechanism of the reduction–hydrodehalogenation reactions leading to the methine clathrochelates.



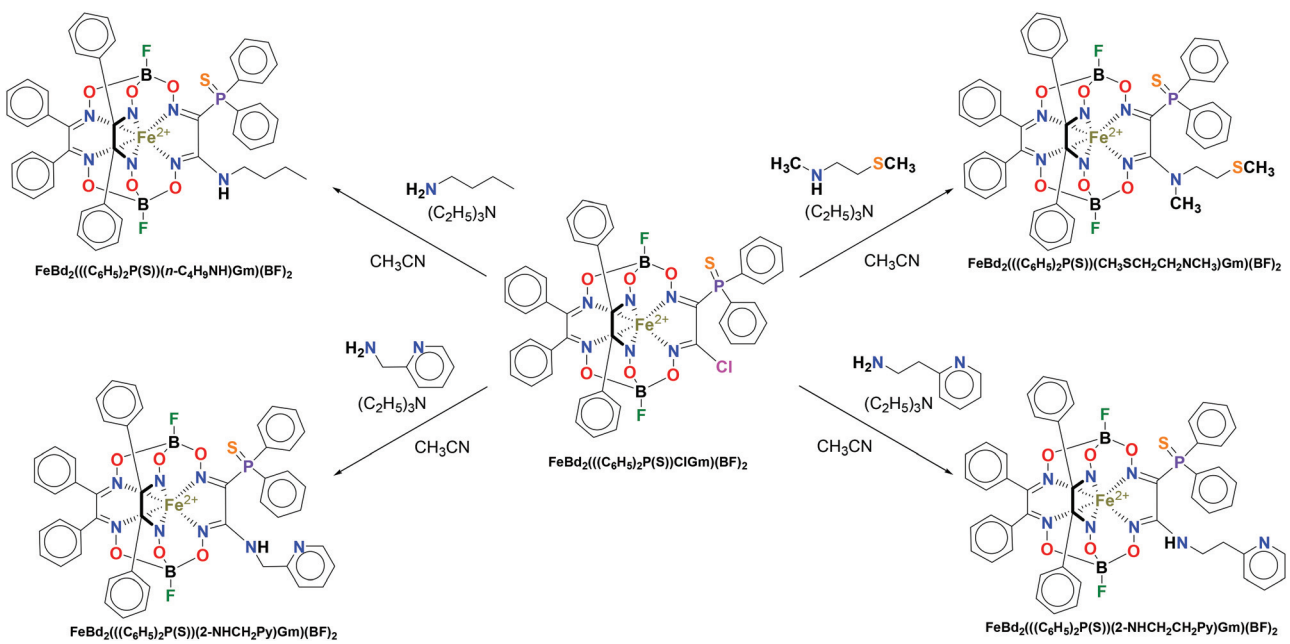
Scheme 2 Most feasible pathway to the thiophosphorylated iron(II) clathrochelates.



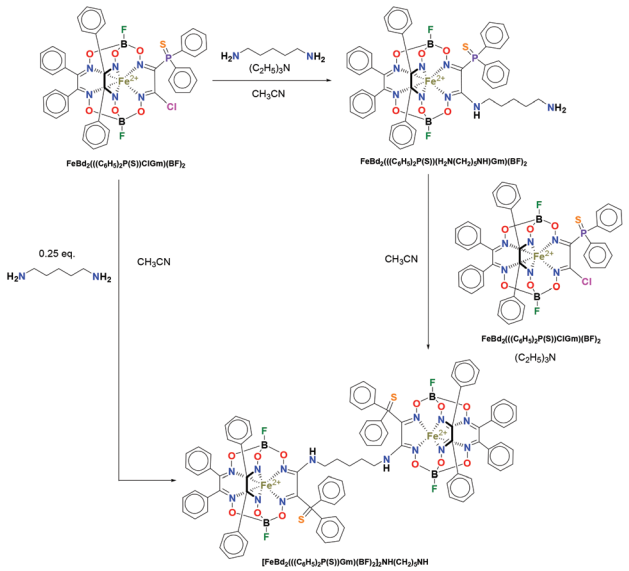
Scheme 3 Nucleophilic substitution of dichloroclathrochelate precursor $FeBd_2(Cl_2Gm)(BF)_2$ with diphenylphosphine sulfide.

nylthiophosphine ribbed substituents in the complex. At the same time, the monochloroclathrochelate $FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$ easily undergoes nucleophilic substitution with sterically unhindered primary and secondary amines under mild reaction conditions by Scheme 4, giving *P,N*-substituted monoribbed-functionalized iron(II) cage complexes in high yields.

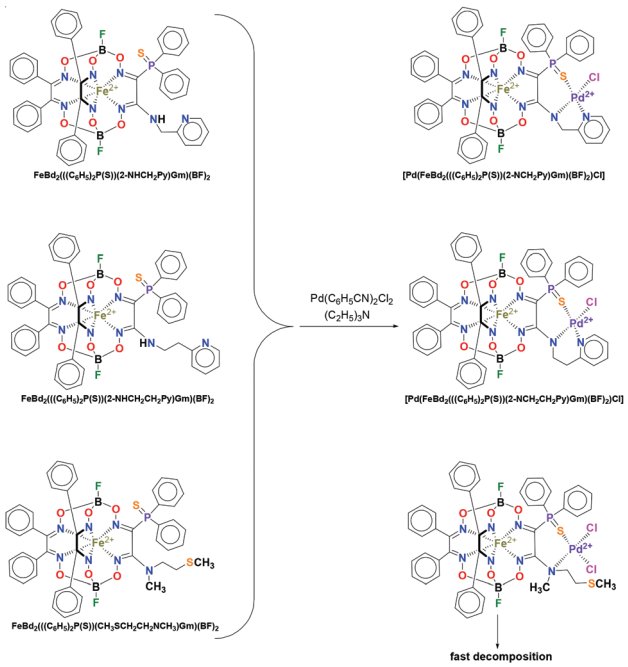
For the synthesis of its bis-clathrochelate derivative $[FeBd_2(((C_6H_5)_2P(S))Gm)(BF)_2]_2(NH(CH_2)_5NH)$, two synthetic strategies were used (Scheme 5): the first one is based on the interaction of an excess of this monochloroclathrochelate precursor with cadaverine, while the other uses the nucleophilicity of the initially synthesized clathrochelate $FeBd_2(((C_6H_5)_2P(S))(H_2N(CH_2)_5NH)Gm)(BF)_2$ with a terminal amino group.



Scheme 4 Synthesis of *P,N*-substituted monoribbed-functionalized iron(II) cage complexes.



Scheme 5 Synthesis of the thiophosphorylated bis-clathrochelate $[FeBd_2(((C_6H_5)_2P(S))Gm)(BF)_2]_2(NH(CH_2)_5NH)$.



Scheme 6 Synthesis of the Pd,Fe-binuclear complexes of N,S-donor macrobicyclic ligands.

Both these synthetic approaches gave the target bis-clathrochelate $[FeBd_2(((C_6H_5)_2P(S))Gm)(BF)_2]_2(NH(CH_2)_5NH)$ under mild reaction conditions (room temperature, acetonitrile as a solvent) in high yields.

Two of the complexes obtained (*i.e.* $FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2Py)Gm)(BF)_2$ and $FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2CH_2Py)Gm)(BF)_2$) contain two strongly donor centers per a clathrochelate molecule (sulfur atom of the diphenylthiophosphine group and nitrogen atom of the pyridyl moiety), and they were used as the macrobicyclic ligands toward palladium(II) ion (Scheme 6). The resulting Pd,Fe-binuclear 1 : 1 complexes were isolated in high yields and then tested as potent catalysts of the Suzuki cross-coupling reaction (*vide infra*). The relative stability of these complexes can be explained by the high donor ability of the above ribbed substituents, as well as by the disposition of their donor centers, allowing them to form thermodynamically favorable[16] five- and six-membered chelate cycles.

In the case of their macrobicyclic analog $FeBd_2(((C_6H_5)_2P(S))(CH_3SCH_2CH_2NCH_3)Gm)(BF)_2$, its palladium(II) complex was detected in solution only; we failed to isolate it in the solid state due to a fast decomposition. The potent donor amino group of this *N*,*P*-substituted macrobicyclic complex has a substantial amide character as a result of its conjugation with a polyazomethine *quasi*-aromatic cage framework[17] and, therefore, a poor donor ability, while the two sulfur atoms belonging to different ribbed substituents are far from each other and cannot form a stable chelate cycle.

The complexes obtained were characterized using elemental analysis, MALDI-TOF mass spectrometry, IR, UV-vis, ^1H, ^{11}B, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopies and by X-ray diffraction.

The thiophosphorylated *P*,*Cl*- and *P*,*N*-substituted ribbed-functionalized mono- and bis-clathrochelates $FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$, $FeBd_2(((C_6H_5)_2P(S))(n\text{-}C_4H_9NH)Gm)(BF)_2$, $FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2Py)Gm)(BF)_2$, $FeBd_2(((C_6H_5)_2P(S))(CH_3SCH_2CH_2NCH_3)Gm)(BF)_2$ and $[FeBd_2(((C_6H_5)_2P(S))Gm)(BF)_2]_2(NH(CH_2)_5NH)$ as well as the palladium(II) complexes $[Pd\text{-}(FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2Py)Gm)(BF)_2)Cl]$ and $[Pd(FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2CH_2Py)Gm)(BF)_2)Cl]$ with N,S-donor macrobicyclic ligands are shown in Fig. 1–7; the main geometrical parameters of the FeN_6 and PdN_2ClS coordination polyhedra and those of the clathrochelate frameworks are listed in Tables 1 and 2. The average Fe–N distances in all the compounds analyzed fall within 1.905–1.915 Å, which is characteristic of low-spin iron(II) complexes. The encapsulated iron(II) ions are situ-

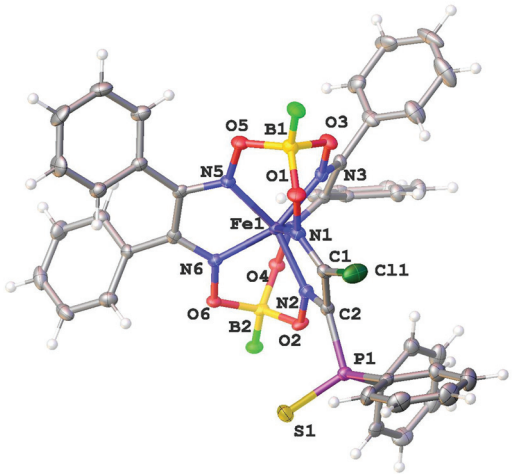


Fig. 1 General view of clathrochelate $FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$. Hereafter, the non-hydrogen atoms are represented as thermal ellipsoids (p = 50%).

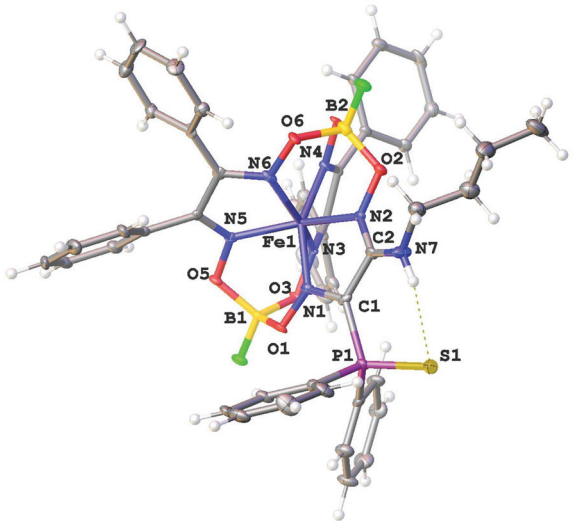


Fig. 2 General view of *P,N*-substituted ribbed-functionalized clathrochelate $FeBd_2(((C_6H_5)_2P(S))(n\text{-}C_4H_9NH)Gm)(BF)_2$; intramolecular N–H···S bond is depicted as a dashed line.

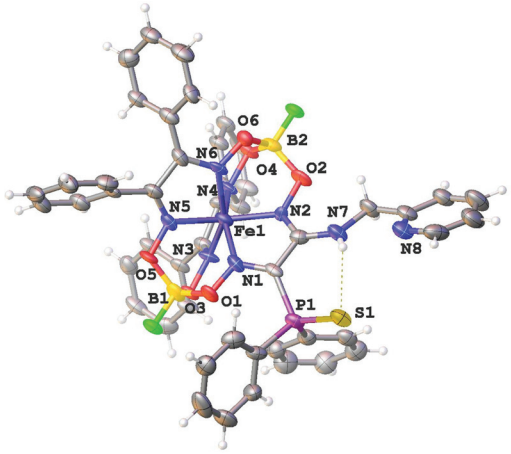


Fig. 3 General view of *P,N*-substituted ribbed-functionalized clathrochelate $FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2Py)Gm)(BF)_2$; intramolecular N–H···S bond is depicted as a dashed line.

ated almost in the centres of their FeN_6-coordination polyhedra, although 0.02–0.03 Å shifted (with an exception of one complex $FeBd_2(((C_6H_5)_2P(S))(CH_3SCH_2CH_2NCH_3)Gm)(BF)_2$) along their B···Fe···B C_3-pseudoaxes in the direction of the N2–N4–N6 triangular bases formed by two phenyl-containing donor oxime groups and a phosphorylated moiety.

The FeN_6 coordination polyhedra possess a similar distorted trigonal prismatic (TP) – trigonal antiprismatic (TAP) geometry (the distortion angle $\varphi = 0°$ for a TP and $\varphi = 60°$ for a TAP). The φ values for the previously reported monoribbed-functionalized bis-α-benzyldioximate iron(II) clathrochelates[10i,j,18] vary from 21 to 24° with the heights h of these TP – TAP polyhedra being 2.33 Å. Among the thiophosphorylated bis-α-benzyldioximate iron(II) mono- and bis-clathrochelates obtained, these characteristic values were observed only in the

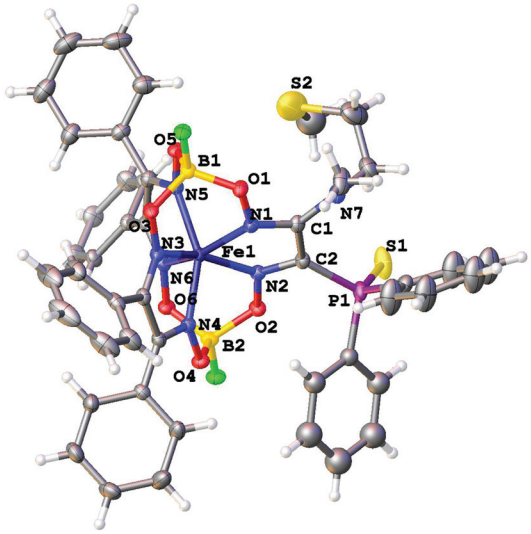


Fig. 4 General view of *P,N*-substituted ribbed-functionalized clathrochelate $FeBd_2(((C_6H_5)_2P(S))(CH_3SCH_2CH_2NCH_3)Gm)(BF)_2$. Only one of two disordered methyl and phenyl moieties is shown.

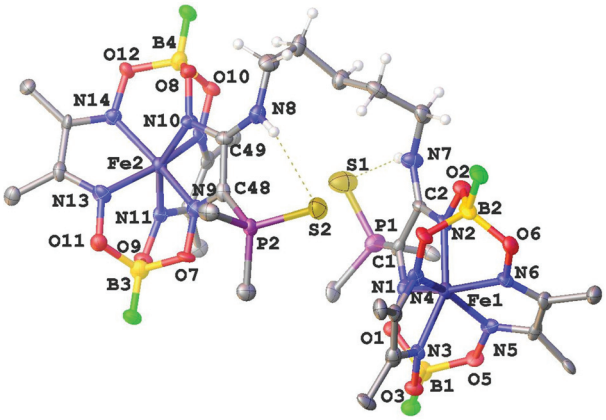


Fig. 5 General view of bis-clathrochelate $[FeBd_2(((C_6H_5)_2P(S))Gm)(BF)_2]_2(NH(CH_2)_5NH)$ (its phenyl substituents are shown as grey balls for clarity); intramolecular N–H···S bonds are shown as dashed lines.

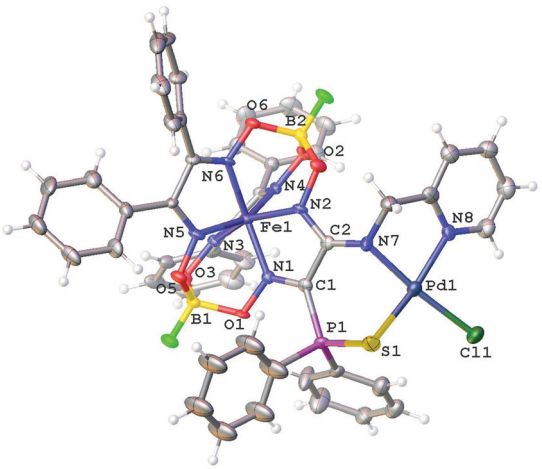


Fig. 6 General view of the palladium(II) complex $[Pd(FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2Py)Gm)(BF)_2)Cl]$ with a N,S-donor macrobicyclic ligand.

case of the monothiophosphorylated precursor $FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$. The φ and h values for *P,N*-substituted mono- and bis-clathrochelates and their palladium(II) complexes vary from 25.8 to 28.6° and from 2.29 to 2.32 Å, respectively. At the same time, the bite angles α (half of the chelate N–Fe–N angle) are similar for all these X-rayed bis-α-benzyldioximate iron(II) clathrochelates (approximately 39°); so an additional TAP distortion of *P,N*-substituted cage complexes is caused by intramolecular interactions. Thus, N–H···S intramolecular interactions with r(N···S) from 3.16(1) to 3.22(1) Å and N–H–S angles from 139 to 152° were found in mono- and bis-clathrochelate molecules $FeBd_2(((C_6H_5)_2P(S))(n\text{-}C_4H_9NH)Gm)(BF)_2$, $FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2Py)Gm)(BF)_2$ and $[FeBd_2(((C_6H_5)_2P(S))Gm)(BF)_2]_2(NH(CH_2)_5NH)$, while the relatively rigid five- (PdN_2C_2) and six-membered ($PdNC_2PS$ or PdN_2C_3) cycles are formed in the case of the complexes $[Pd(FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2Py)Gm)(BF)_2)Cl]$ and $[Pd(FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2CH_2Py)Gm)(BF)_2)Cl]$. In contrast, only weak intramolecular Cl···π interaction was found in a crystal of monothiophosphorylated precursor $FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$; for its diphenylthiophosphoryl group the dihedral angle between the mean planes of one of the phenyl substituents and that of the Cl1–C1–C2–P1 moiety is equal to 67.4(3)°, and the distance from Cl1 atom to the mean plane is approximately 3.15(1) Å. Characteristics of the clathrochelate framework in $FeBd_2(((C_6H_5)_2P(S))(CH_3SCH_2CH_2NCH_3)Gm)(BF)_2$ are intermediate between that of its monochloroclathrochelate precursor and those of other *P,N*-substituted cage compounds.

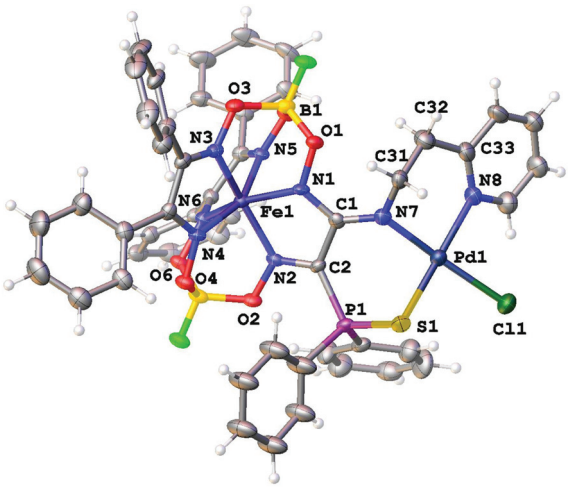


Fig. 7 General view of the palladium(II) complex $[Pd(FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2CH_2Py)Gm)(BF)_2)Cl]$ with a N,S-donor macrobicyclic ligand.

The coordination of the thiophosphoryl groups of macrobicyclic ligands $FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2Py)Gm)(BF)_2$ and $(FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2CH_2Py)Gm)(BF)_2)$ to palladium(II) ion causes the elongation of their P═S bonds from approximately 1.95 to 1.99 Å. The five-membered Pd-containing chelate cycle in $[Pd(FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2Py)Gm)(BF)_2)Cl]$ has an envelope conformation, with the donor nitrogen atom N7 deviating by 0.70(2) Å. The six-membered $PdNC_2PS$ and PdN_2C_3 chelate cycles in both the palladium complexes $[Pd(FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2Py)Gm)(BF)_2)Cl]$ and $[Pd(FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2CH_2Py)Gm)(BF)_2)Cl]$ have a half-chair conformation. The palladium and sulfur atoms are deviated by −1.03(1)/−0.89(1) and 0.41(1)/0.62(1) Å from the mean planes of their $PdNC_2PS$ cycles, while in the case of PdN_2C_3 cycles the N7 and C31 atoms are deviated by −0.69(1) and 0.18(1) Å, respectively. In both these complexes, the palladium(II) ion has a twisted square-planar N_2SCl-coordination environment with the dihedral angles between their Pd1–N7–N8 and Pd1–Cl1–S1 planes of approximately 8.9(4) and 6.9(3)°, respectively.

Table 1 Main geometrical parameters of the monothiophosphorylated iron(II) clathrochelate precursor and its *P,N*-substituted bis-macrobicyclic derivative

Parameter	$FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$	$[FeBd_2(((C_6H_5)_2P(S))Gm)(BF)_2]_2$ $(NH(CH_2)_5NH)$	
Metal ion	Fe^{2+}	$Fe^{2+}(1)$	$Fe^{2+}(2)$
M–N (Å)	1.897(3)–1.925(3)	1.902(4)–1.916(4)	1.893(4)–1.932(4)
	av. 1.915	*av.* 1.909	*av.* 1.907
Fe1···B1 (Å)	2.993(5)	2.960(7)	2.957(7)
Fe1···B2 (Å)	2.978(5)	2.987(7)	2.958(7)
N–O (Å)	1.349(4)–1.379(4)	1.373(5)–1.417(5)	1.343(5)–1.394(5)
	av. 1.369	*av.* 1.386	*av.* 1.373
B–O (Å)	1.471(4)–1.490(5)	1.464(7)–1.515(7)	1.476(7)–1.499(7)
	av. 1.484	*av.* 1.485	*av.* 1.487
C═N (Å)	1.302(5)–1.328(5)	1.288(6)–1.348(7)	1.306(7)–1.345(7)
	av. 1.313	*av.* 1.316	*av.* 1.324
C–C (Å)	1.449(6)–1.457(6)	1.449(7)–1.498(7)	1.437(7)–1.481(8)
	av. 1.454	*av.* 1.463	*av.* 1.455
P═S (Å)	1.946(2)	1.933(3)	1.953(2)
N═C–C═N (°)	8.0(7)–12.1(7)	6.2(5)–9.0(5)	8.1(5)–14.8(5)
	av. 9.6	*av.* 7.9	*av.* 11.6
φ (°)	24.0	26.0	28.6
α (°)	39.2	39.0	39.2
h (Å)	2.34	2.30	2.29

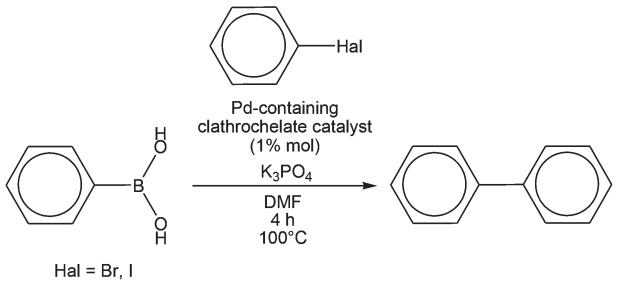
Table 2 Main geometrical parameters of *P,N*-substituted iron(II) clathrochelates and their complexes with palladium(II) ion

Parameter	$FeBd_2(((C_6H_5)_2P(S))$-$(n\text{-}C_4H_9NH)Gm)(BF)_2$		$FeBd_2(((C_6H_5)_2P(S))$-$(CH_3SCH_2CH_2NCH_3)Gm)$ $(BF)_2$		$FeBd_2(((C_6H_5)_2P(S))$-$(2\text{-}NHCH_2Py)Gm)(BF)_2$		[Pd($FeBd_2(((C_6H_5)_2P(S))$-P(S)) $(2\text{-}NCH_2Py)Gm)(BF)_2$Cl]		[Pd($FeBd_2(((C_6H_5)_2P(S))$-$(2\text{-}NCH_2CH_2Py)Gm)$-$(BF)_2$Cl]	
Metal ion	Fe^{2+}		Fe^{2+}		Fe^{2+}	Pd^{2+}	Fe^{2+}	Pd^{2+}	Fe^{2+}	Pd^{2+}
M–N (Å)	1.901(3)–1.933(5)		1.890(3)–1.931(3)		1.887(7)–1.934(7)	1.876(7)–1.921(7)	1.977(7)–2.033(8)		1.884(5)–1.920(5)	1.986(6)–2.091(6)
	av. 1.914		*av.* 1.908		*av.* 1.914	*av.* 1.905	*av.* 2.008		*av.* 1.905	*av.* 2.039
M–Cl (Å)							2.305(3)			2.312(2)
M–S (Å)							2.293(3)			2.290(2)
Fe1···B1 (Å)	2.982(8)		2.968(4)		2.96(1)	2.97(1)			2.969(8)	
Fe1···B2 (Å)	2.951(8)		2.971(4)		2.93(1)	2.95(1)			2.941(8)	
N–O (Å)	1.357(6)–1.391(6)		1.359(3)–1.380(3)		1.346(8)–1.417(8)	1.366(9)–1.405(9)			1.367(96–1.408(6)	
	av. 1.375		*av.* 1.368		*av.* 1.373	*av.* 1.378			*av.* 1.379	
B–O (Å)	1.466(8)–1.513(8)		1.460(4)–1.499(4)		1.44(1)–1.50(1)	1.47(1)–1.50(1)			1.467(8)–1.503(8)	
	av. 1.489		*av.* 1.481		*av.* 1.48	*av.* 1.48			*av.* 1.484	
C=N (Å)	1.297(7)–1.329(7)		1.299(4)–1.310(4)		1.29(1)–1.36(1)	1.30(1)–1.33(1)			1.296(8)–1.320(18)	
	av. 1.311		*av.* 1.306		*av.* 1.31	*av.* 1.31			*av.* 1.312	
C–C (Å)	1.460(8)–1.479(8)		1.453(4)–1.468(4)		1.44(1)–1.49(1)	1.44(1)–1.50(1)			1.46(1)–1.49(1)	
	av. 1.470		*av.* 1.459		*av.* 1.46	*av.* 1.47			*av.* 1.47	
P=S (Å)	1.951(2)		1.934(3)		1.949(3)	1.994(4)			1.996(3)	
N=C–C=N (°)	12.6(7)–15.9(7)		7.8(3)–18.9(4)		0.0(7)–13.0(7)	6.3(6)–12.8(6)			11.1(5)–13.4(5)	
	av. 14.7		*av.* 12.8		*av.* 8.5	*av.* 10.6			*av.* 12.0	
φ (°)	26.0		25.8		26.9	27.6			28.4	
α (°)	38.9		39.2		39.1	39.1			39.1	
h (Å)	2.31		2.32		2.31	2.29			2.29	

The number and position of the signals in the solution ^1H, $^{11}B\{^1H\}$, $^{19}F\{^1H\}$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the diamagnetic monoribbed-functionalized iron(II) complexes synthesized as well as the ratios of the integral intensities of protons of their chelate α-benzyldioximate fragments and those of the ribbed *P*- and *N*-substituents in the ^1H NMR spectra confirmed the composition and symmetry of these thiophosphorylated and *P,N*-substituted mono- and bis-clathrochelates as well as their complexes as N,S-donor macrobicyclic ligands with palladium(II) ion. In their $^{13}C\{^1H\}$ NMR spectra, the signals of four types of the azomethine carbon atoms are observed indicating the absence of a symmetry plane that passes through the middles of the chelate C–C bonds in the α-dioximate fragments and the encapsulated iron(II) ion. The $^{11}B\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra also suggest non-equivalence of their tetrahedral O_3BF capping fragments. In the case of N,S-donor clathrochelate ligand $FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2Py)Gm)(BF)_2$ with a methylene bridging fragment, its coordination to the palladium(II) ion, followed by the deprotonation of the amino group and the formation of a five-membered PdN_2C_2 chelate cycle, resulted in the substantial (up to 12 ppm) shifts of the ^{13}C NMR signals of these carbon atoms. The same effect of the coordination to Pd^{2+} ion is observed for the diphenylphosphine sulfide donor group in the $^{31}P\{^1H\}$ NMR spectrum of this complex.

In contrast, for the macrobicyclic ligand $FeBd_2(((C_6H_5)_2P(S))$-$(2\text{-}NHCH_2CH_2Py)Gm)(BF)_2$ with an ethylene spacer fragment forming a six-membered PdN_2C_3 cyclic moiety, the changes in the $^{13}C\{^1H\}$ NMR spectrum after its coordination to this ion are small, whereas the $^{31}P\{^1H\}$ NMR signal of its thiophosphoryl donor group undergoes almost the same shift (approximately 3.5 ppm) as in the case of the methylene-bridged complex $FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2Py)Gm)(BF)_2$.

While the deconvoluted solution UV-vis spectrum of the iron(II) dichloroclathrochelate precursor contains three intensive bands in the visible region from 400 to 470 nm assigned to the metal-to-ligand Fe*d*→Lπ^* charge transfer (MLCT) bands in the highly π-conjugated polyazomethine macrobicyclic framework, two new bands at 500 and 515 nm appear in the spectrum of its monothiophosphorylated derivative $FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$ (see ESI, Table S3¶). The latter may be caused by the electron-donating diphenylphosphine sulfide substituent in its ribbed chelate fragment. Further functionalization of this monochloroclathrochelate precursor with the electron-donating amine substituents leads to a substantial (by approximately 20–30 nm) longwave-shift of the band at 515 nm. The coordination of clathrochelates $FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2CH_2Py)Gm)(BF)_2$ and $FeBd_2$-$(((C_6H_5)_2P(S))(2\text{-}NHCH_2Py)Gm)(BF)_2$ to the palladium(II) ion led to the additional longwave-shift of this band by 10 and 40 nm and the appearance of a new band at 577 and 605 nm, respectively. These facts are indicative of a dramatic redistribution of the electron density in the π-conjugated clathrochelate framework caused by its ribbed functionalization with diphenylphosphine sulfide and amine substituents as well as by their further coordination to the palladium ion.



Scheme 7 Suzuki cross-coupling reaction in the presence of the Pd, Fe-binuclear complexes.

Table 3 Yields of Suzuki cross-coupling reactions catalyzed by the palladium(II) complexes with N,S-donor clathrochelate ligands

Catalyst	Substrate	Conversion (%)
$[Pd(FeBd_2(((C_6H_5)_2P(S))$-$(2\text{-}NCH_2CH_2Py)Gm)(BF)_2)Cl]$	C_6H_5I	>99
$[Pd(FeBd_2(((C_6H_5)_2P(S))$-$(2\text{-}NCH_2Py)Gm)(BF)_2)Cl]$	C_6H_5I	98
$[Pd(FeBd_2(((C_6H_5)_2P(S))$-$(2\text{-}NCH_2CH_2Py)Gm)(BF)_2)Cl]$	C_6H_5Br	78
$[Pd(FeBd_2(((C_6H_5)_2P(S))$-$(2\text{-}NCH_2Py)Gm)(BF)_2)Cl]$	C_6H_5Br	71

The maxima in the spectra of the monoclathrochelate $FeBd_2(((C_6H_5)_2P(S))(H_2N(CH_2)_5NH)Gm)(BF)_2$ with the terminal amino group and its bis-clathrochelate derivative $[FeBd_2(((C_6H_5)_2P(S))Gm)(BF)_2]_2(NH(CH_2)_5NH)$ are very similar, suggesting the absence of electronic interactions between the FeN_6 chromophores in this ditopic molecule with a labile alkyl spacer. At the same time, the intensities of its MLCT bands are approximately two times higher than those for the initial monoclathrochelate, due to the presence of two such chromophores per bis-clathrochelate molecule of $[FeBd_2(((C_6H_5)_2P(S))Gm)(BF)_2]_2(NH(CH_2)_5NH)$. The spectra of all these clathrochelates also contain intensive bands in the UV region, assigned to the π,π*-transitions both in the π-conjugated α-dioximate chelate fragments of their macrobicyclic ligands and in the functionalizing ribbed substituents.

The palladium(II) complexes $[Pd(FeBd_2(((C_6H_5)_2P(S))$-$(2\text{-}NCH_2CH_2Py)Gm)(BF)_2)Cl]$ and $[Pd(FeBd_2(((C_6H_5)_2P(S))$-$(2\text{-}NCH_2Py)Gm)(BF)_2)Cl]$ were studied as potent catalysts of the model Suzuki cross-coupling reaction of iodobenzene with phenylboronic acid in a DMF solution at 100 °C for 4 h using K_3PO_4 as an inorganic base (Scheme 7).

In both cases, very high conversion of iodobenzene to biphenyl was observed (Table 3). To further evaluate their catalytic activity, a less reactive bromobenzene was used as a substrate. As it can be seen from Table 3, the palladium(II) complex of clathrochelate ligand $FeBd_2(((C_6H_5)_2P(S))$-$(2\text{-}NCH_2CH_2Py)Gm)(BF)_2$, with the ethylene spacer fragment forming a six-membered PdN_2C_3 chelate cycle showed a better conversion in this system as compared with its methylene-containing analog $FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2Py)Gm)(BF)_2$ giving the five-membered PdN_2C_2 cyclic moiety.

Conclusions

We successfully performed the phosphorylation of a cage metal complex giving the first monophosphorylated iron(II) clathrochelate. This complex undergoes further nucleophilic substitution with aliphatic mono- and diamines, leading to *P*,*N*-substituted mono- and bis-clathrochelates. Those with the donor diphenylthiophosphine and pyridyl groups form Pd,Fe-binuclear 1 : 1 complexes, which were found to be efficient and structure-dependent catalysts of the Suzuki cross-coupling reaction.

Experimental section

General considerations

The reagents used, $FeCl_2{\cdot}4H_2O$, α-benzyldioxime (denoted as H_2Bd), $BF_3{\cdot}O(C_2H_5)_2$, diphenylphosphine sulfide, triethylbenzylammonium chloride, *n*-butylamine, 2-aminomethylpyridine, 2-aminoethylpyridine, *N*-methyl-2-(methylthio)-ethylamine, cadaverine, complex $Pd(C_6H_5CN)_2Cl_2$, triethylamine, sorbents, acids, bases, and organic solvents were obtained commercially (SAF). The dichloroglyoxime (denoted as Cl_2GmH_2) was prepared by chlorination of glyoxime as described in ref. 19. The dichloroclathrochelate precursor $FeBd_2(Cl_2Gm)(BF)_2$ was obtained as described elsewhere.[10b]

Analytical data (C, H, N content) were obtained with a Carlo Erba model 1106 microanalyzer. The iron and phosphorus content were determined spectrophotometrically. The sulfur content was determined by titrimetry, using the Shoeniger method.

MALDI-TOF mass spectra were recorded in both the positive and the negative spectral regions using a MALDI-TOF-MS Bruker Autoflex mass spectrometer in the reflecto-mol mode. The ionization was induced by a UV-laser with a wavelength of 336 nm. The sample was applied to a nickel plate, and 2,5-dihydroxybenzoic acid was used as a matrix. The accuracy of the measurements was 0.1%.

IR spectra of the solid sample (KBr tablets) in the range 400–4000 cm^{-1} were recorded with a Nicolet Magna-IR 750 FTIR-spectrophotometer.

UV-vis spectra of the solutions in dichloromethane were recorded in the range 230–800 nm with a Lambda 9 Perkin Elmer spectrophotometer. The individual Gaussian components of these spectra were calculated using the SPECTRA program.

^1H, $^{11}B\{^1H\}$, $^{19}F\{^1H\}$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the complexes obtained were recorded from their CD_2Cl_2 solutions using a Bruker *Avance 400* spectrometer.

Synthesis

$FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$. Complex $FeBd_2(Cl_2Gm)$-$(BF)_2$ (1 g, 1.34 mmol), diphenylphosphine sulfide (0.345 g, 1.58 mmol), and triethylbenzylammonium chloride (0.018 g, 5 mol%) were dissolved in dichloromethane (10 ml) and 50% NaOH aqueous solution (0.45 g) was added dropwise to the

vigorously stirring reaction mixture. The reaction mixture was stirred for 1.5 h, then diluted with dichloromethane (30 ml) and washed with water (30 ml, in two portions). The dichloromethane solution was evaporated to dryness and purified by preparative TLC on silica gel (the gradient eluents: hexane–dichloromethane 1 : 1–1 : 4 mixtures). The major elute was evaporated to dryness, washed with hexane and dried *in vacuo*. Yield: 1.075 g (86%). *Anal. Calc.* for $C_{42}H_{30}N_6O_6B_2ClF_2FePS$ (%): C, 54.32; H, 3.26; N, 9.05; S, 3.45. Found (%): C, 54.19; H, 3.29; N, 8.95; S, 3.32. MS (MALDI-TOF) *m*/*z* (I, %): (positive range) 929 (100) $[M]^{+\bullet}$, 952 (15) $[M + Na^+]^+$, 968 (5) $[M + K^+]^+$; (negative range) −929 $[M]^{-\bullet}$. ^{1}H NMR (CD_2Cl_2): δ, ppm; *J*, Hz: 7.15–7.30 (m, 20H, Ph(Bd)), 7.35–7.45 (m, 4H, *meta*-H (PhP)), 7.45–7.55 (m, 2H, *para*-H (PhP)), 7.85 (dd, 4H, *ortho*-H (Ph-P), $^3J_{^1H-^1H}$ = 7.8, $^3J_{^1H-^{31}P}$ = 14.6). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 128.67 (s, *ortho*-Ph(Bd)), 129.37 (s, *ipso*-Ph(Bd)), 129.31 (s, ClC═N), 129.32 (d, $^3J_{^{13}C-^{31}P}$ = 13.6, *meta*-PhP), 131.11 (s, *para*-Ph-(Bd)), 131.17 (s, *meta*-Ph(Bd)), 131.27 (d, $^1J_{PC}$ = 91.3, *ipso*-C in C_6H_5P), 132.09 (d, $^2J_{PC}$ = 11.4, *ortho*-C_6H_5P), 132.96 (d, $^4J_{^{13}C-^{31}P}$ = 3.0, *para*-PhP), 151.71 (d, $^1J_{^{13}C-^{31}P}$ = 69.42, PC═N), 159.36, 159.81 (both s, PhC═N). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ, ppm: 32.01. ^{19}F{^{1}H} NMR (CD_2Cl_2) δ, ppm; *J*, Hz: −168.40, −169.30 (both q, $^1J_{^{11}B-^{19}F}$ = 16.0). ^{11}B{^{1}H} NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 3.25, 3.71 (both d, $^1J_{^{11}B-^{19}F}$ = 16.0). IR (KBr) ν/cm^{-1}: 920, 931, 943, 1067, 1108, 1158 ν(N–O), 1220 m ν(B–O) + ν(B–F), 1549, 1580 ν(C═N). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} L cm^{-1}): 262(33), 299(11), 355(4.0), 412(4.4), 441(7.7), 467(19), 499(15), 514(2.9).

$FeBd_2(((C_6H_5)_2P(S))(n\text{-}C_4H_9NH)Gm)(BF)_2$. Complex $FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$ (0.1 g, 0.108 mmol) was dissolved/suspended in acetonitrile (2 ml) and *n*-butylamine (0.2 g, 2.74 mmol) was added to the stirred solution. The reaction mixture was stirred for 12 h and left overnight. The precipitate formed was filtered off, washed with acetonitrile (1 ml) and dichloromethane (1 ml), and dried *in vacuo*. Yield: 0.099 g (95%). *Anal. Calc*. for $C_{46}H_{40}N_7O_6B_2F_2FePS$ (%): C, 57.23; H, 4.18; N, 10.16. Found (%): C, 57.32; H, 4.24; N, 10.28. MS (MALDI-TOF) *m*/*z* (I, %): 965 (100) $[M]^{+\bullet}$, 988 (10) $[M + Na^+]^+$, 1004 (15) $[M + K^+]^+$. ^{1}H NMR (CD_2Cl_2): δ, ppm; *J*, Hz: 0.86 (m, 3H, CH_3, $^3J_{^1H-^1H}$ = 7.3), 1.29 (sextet, 2H, CH_2CH_3, $^3J_{^1H-^1H}$ = 7.6), 1.49 (pentet, 2H, $CH_2CH_2CH_3$, $^3J_{^1H-^1H}$ = 7.4), 3.78 (q, 2H, CH_2NH, $^3J_{^1H-^1H}$ = 7.4), 7.22–7.42 (m, 20H, Ph(Bd)), 7.45–7.60 (m, 6H, *meta*- + *para*-PhP), 7.88 (dd, 4H, *ortho*-PhP, $^3J_{^1H-^1H}$ = 7.4, $^3J_{^1H-^{31}P}$ = 14.8), 8.36 (m, 1H, NH, $^3J_{^1H-^1H}$ = 5.3). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 13.71 (s, CH_3), 19.80 (s, CH_2CH_3), 32.58 (s, $CH_2CH_2CH_3$), 45.79 (s, CH_2NH), 127.73, 127.82 (both s, *ortho*-Ph(Bd)), 128.62 (d, $^3J_{^{13}C-^{31}P}$ = 13.9, *meta*-PhP), 128.87, 129.19 (both s, *ipso*-Ph(Bd)), 129.84 (s, *para*-Ph(Bd)), 130.40 (s, *meta*-Ph(Bd)), 130.68 (d, $^1J_{^{13}C-^{31}P}$ = 91.3, *ipso*-PhP), 130.78 (s, *meta*-Ph(Bd)), 131.63 (d, $^2J_{^{13}C-^{31}P}$ = 12.1, *ortho*-PhP), 132.44 (d, $^4J_{^{13}C-^{31}P}$ = 3.3, *para*-PhP), 142.33 (d, $^1J_{^{13}C-^{31}P}$ = 64.9, PC═N), 151.94 (d, $^2J_{^{13}C-^{31}P}$ = 16.9, NHC═N), 155.72, 157.68 (both s, PhC═N). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ, ppm: 34.68. ^{19}F{^{1}H} NMR (CD_2Cl_2) δ, ppm; *J*, Hz: −167.50, −169.04 (both q, $^1J_{^{11}B-^{19}F}$ = 12.0). ^{11}B{^{1}H} NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 3.41, 3.74 (both d, $^1J_{^{11}B-^{19}F}$ = 12.0). IR (KBr) ν/cm^{-1}: 911, 941, 1060, 1109, 1176 ν(N–O), 1210 m ν(B–O) + ν(B–F), 1547, 1581 ν(C═N). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} L cm^{-1}): 256(23), 283(15), 300(11), 356(3.4), 414(3.9), 465(8.2), 496(20), 542(6.6).

$FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2Py)Gm)(BF)_2$. Complex $FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$ (0.1 g, 0.108 mmol) was dissolved/suspended in acetonitrile (2 ml) and 2-aminomethylpyridine (0.014 g, 0.129 mmol) and triethylamine (0.018 ml, 0.129 mmol) were added. The reaction mixture was stirred for 12 h and evaporated to dryness. The solid residue was washed with water (5 ml) and extracted with dichloromethane (10 ml, in two portions). The dichloromethane solution was evaporated to dryness and purified by preparative TLC on silica gel (the gradual eluents: dichloromethane–hexane 1 : 1–10 : 1 mixtures). The major elute was evaporated to dryness, washed with hexane and dried *in vacuo*. Yield: 0.093 g (88%). *Anal. Calc.* for $C_{48}H_{37}N_8O_6B_2F_2FePS$ (%): C, 57.63; H, 3.73; N, 11.20; S, 3.21. Found (%): C, 57.52; H, 3.84; N, 11.17; S, 2.98. MS (MALDI-TOF) *m*/*z* (I, %): 1000 (80) $[M]^{+\bullet}$, 1023 (90) $[M + Na^+]^+$, 1039 (100) $[M + K^+]^+$. ^{1}H NMR (CD_2Cl_2): δ, ppm; *J*, Hz: 5.11 (d, 2H, CH_2NH, $^3J_{^1H-^1H}$ = 5.8), 7.15 (dd, 1H, C^3H(Py), $^3J_{^1H-^1H}$ = 7.2, $^4J_{^1H-^1H}$ = 2.0), 7.25–7.45 (m, 20H + 1H, Ph(Bd) + C^5H (Py)), 7.46–7.65 (m, 6H + 1H, *meta*- + *para*-PhP + C^4H(Py)), 7.91 (dd, 4H, *ortho*-PhP, $^3J_{^1H-^1H}$ = 7.5, $^3J_{^1H-^{31}P}$ = 15.0), 8.47 (d, 1H, C^6H (Py), $^3J_{^1H-^1H}$ = 4.5), 9.04 (m, 1H, NH, $^3J_{^1H-^1H}$ = 5.8). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 50.59 (s, CH_2NH), 121.82 (s, C^3(Py)), 121.95 (s, C^5(Py)), 127.71, 127.81 (both s, *ortho*-Ph(Bd)), 128.50 (d, $^3J_{^{13}C-^{31}P}$ = 13.9, *meta*-PhP), 128.86, 129.17 (both s, *ipso*-Ph (Bd)), 129.84 (s, *para*-Ph(Bd)), 130.40, 130.76 (both s, *meta*-Ph (Bd)), 130.78 (d, $^1J_{^{13}C-^{31}P}$ = 91.3, *ipso*-PhP), 131.70 (d, $^2J_{^{13}C-^{31}P}$ = 12.1, *ortho*-PhP), 132.28 (d, $^4J_{^{13}C-^{31}P}$ = 3.3, *para*-PhP), 136.32 (s, C^4(Py)), 141.83 (d, $^1J_{^{13}C-^{31}P}$ = 63.9, PC═N), 148.76 (s, C^6(Py)), 151.91 (br. s, NHC═N), 155.75 (s, PhC═N), 157.19 (s, C^2(Py)), 157.56 (s, PhC═N). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ, ppm: 34.79. ^{19}F{^{1}H} NMR (CD_2Cl_2) δ, ppm; *J*, Hz: −166.30, −166.80 (both q, $^1J_{^{11}B-^{19}F}$ = 15.0). ^{11}B{^{1}H} NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 3.43, 3.69 (both d, $^1J_{^{11}B-^{19}F}$ = 15.0). IR (KBr) ν/cm^{-1}: 943 m, 1061, 1110, 1175 ν(N–O), 1211 m ν(B–O) + ν(B–F), 1568 ν(C═N), 1591 m ν(C═N) + δ(N–H). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} L cm^{-1}): 256(18), 284(16), 320(3.3), 407(3.1), 469(5.0), 496(12), 533(4.3).

$FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2CH_2Py)Gm)(BF)_2$. This complex was obtained like the previous one except that 2-aminoethylpyridine (0.016 g, 0.130 mmol) was used instead of 2-aminomethylpyridine. The product obtained was purified by preparative TLC on silica gel (eluent: dichloromethane–acetonitrile 10 : 1 mixture). The major elute was evaporated to dryness, washed with hexane and dried *in vacuo*. Yield: 0.061 g (56%). *Anal. Calc.* for $C_{49}H_{39}N_8O_6B_2F_2FePS$ (%): C, 58.02; H, 3.88; N, 11.05; P, 3.05; S, 3.16. Found (%): C, 57.97; H, 3.78; N, 10.90; P, 2.98; S, 3.09. MS (MALDI-TOF) *m*/*z* (I, %): 1014 (100) $[M]^{+\bullet}$, 1037 (60) $[M + Na^+]^+$, 1053 (40) $[M + K^+]^+$. ^{1}H NMR (CD_2Cl_2): δ, ppm; *J*, Hz: 3.14 (m, 2H, CH_2Py, $^3J_{^1H-^1H}$ = 6.6), 4.14 (q, 2H, CH_2NH, $^3J_{^1H-^1H}$ = 6.6), 7.12 (m, 1H, C^3H(Py), $^3J_{^1H-^1H}$ = 5.1), 7.20–7.45 (m, 20H + 1H, Ph(Bd) + C^5H(Py)), 7.46–7.65 (m, 6H + 1H, *meta*- + *para*-PhP + C^4H(Py)), 7.88 (dd, 4H, *ortho*-PhP, $^3J_{^1H-^1H}$ = 7.5, $^3J_{^1H-^{31}P}$ = 14.8), 8.52 (d, 1H, C^6H(Py), $^3J_{^1H-^1H}$ = 3.6), 8.68 (m, 1H, NH, $^3J_{^1H-^1H}$ = 6.6). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 39.65 (s, CH_2Py), 45.21 (s, CH_2NH), 121.29 (s, C^3(Py)),

123.59 (s, C^5(Py)), 127.70, 127.77 (both s, *ortho*-Ph(Bd)), 128.54 (d, $^3J_{^{13}C-^{31}P}$ = 13.9, *meta*-PhP), 128.84, 129.16 (both s, *ipso*-Ph (Bd)), 129.80 (s, *para*-Ph(Bd)), 130.36 (s, *meta*-Ph(Bd)), 130.65 (d, $^1J_{^{13}C-^{31}P}$ = 91.7, *ipso*-PhP), 130.75 (s, *meta*-Ph(Bd)), 131.57 (d, $^2J_{^{13}C-^{31}P}$ = 12.1, *ortho*-PhP), 132.33 (d, $^4J_{^{13}C-^{31}P}$ = 3.3, *para*-PhP), 136.30 (s, C^4(Py)), 142.39 (d, $^1J_{^{13}C-^{31}P}$ = 63.8, PC═N), 149.09 (s, C^6(Py)), 151.76 (d, $^2J_{^{13}C-^{31}P}$ = 18.0, NHC═N), 155.70, 157.66 (both s, PhC═N), 158.66 (s, C^2(Py)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ, ppm: 34.63. $^{19}F\{^1H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: −108.65, −110.24 (both q, $^1J_{^{11}B-^{19}F}$ = 15.0). $^{11}B\{^1H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 3.31, 3.46 (both d, $^1J_{^{11}B-^{19}F}$ = 15.0). IR (KBr) ν/cm^{-1}: 903, 910, 922, 941, 950, 1058, 1111, 1159, 1173 ν(N–O), 1209 m ν(B–O) + ν(B–F), 1544 m ν(C═N) + δ(N–H), 1578 ν(C═N). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} L cm^{-1}): 250(14), 267(3.6), 277(20), 299(4.8), 406(2.7), 490(20), 543(4.6).

$FeBd_2(((C_6H_5)_2P(S))(CH_3SCH_2CH_2NCH_3)Gm)(BF)_2$. Complex $FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$ (0.1 g, 0.108 mmol) was dissolved/suspended in acetonitrile (3 ml) and *N*-methyl-2-(methylthio)ethylamine (0.012 g, 0.110 mmol) and triethylamine (0.015 ml, 0.110 mmol) were added. The reaction mixture was stirred for 12 h and evaporated to dryness. The solid residue was washed with water (5 ml) and extracted with dichloromethane (10 ml, in two portions). The dichloromethane extract was evaporated to dryness and purified by preparative TLC on silica gel (eluent: dichloromethane–hexane 1 : 1 mixture). The major elute was evaporated to dryness, washed with hexane and dried *in vacuo*. Yield: 0.094 g (87%). *Anal. Calc.* for $C_{46}H_{40}N_7O_6B_2F_2FePS_2$ (%): C, 55.39; H, 4.04; N, 9.83. Found (%): C, 55.30; H, 3.90; N, 9.69. MS (MALDI-TOF) *m*/*z* (I, %): (positive range) 625 (100) $[M–((Ph_2PS)(MeS(CH_2)_2NMe)Gm–O)]^{+\bullet}$, 740 (40) $[M–Ph_2PS–2\ Me]^{+\bullet}$; (negative range) – 676 (100) $[M–Ph_2PS–MeS(CH_2)_2NMe]^{-\bullet}$, −840 (25) $[M + DHB–Ph_2PS–MeS(CH_2)_2NMe]^{-\bullet}$. ^1H NMR (CD_2Cl_2): δ, ppm; *J*, Hz: 2.12 (s, 3H, CH_3S), 2.78 (s, 3H, CH_3N), 2.66 (m, 2H, CH_2S, $^3J_{^1H-^1H}$ = 6.6), 3.15 (br. s, 2H, CH_2N), 7.35–7.50 (m, 20H, Ph(Bd)), 7.58–7.68 (m, 6H, *meta*- + *para*-PhP), 8.09 (dd, 4H, *ortho*-PhP, $^3J_{^1H-^{31}P}$ = 7.6, $^3J_{^1H-^{31}P}$ = 15.0). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 15.27 (s, SCH_3), 32.33 (s, CH_2S), 39.21 (s, NCH_3), 55.30 (s, CH_2N), 127.90 (s, *ortho*-Ph(Bd)), 128.36 (d, $^3J_{^{13}C-^{31}P}$ = 13.2, *meta*-PhP), 129.03, 129.13 (both s, *ipso*-Ph(Bd)), 130.12 (s, *para*-Ph(Bd)), 130.35, 130.56 (both s, *meta*-Ph(Bd)), 130.46 (d, $^1J_{^{13}C-^{31}P}$ = 91.6, *ipso*-PhP), 130.90 (d, $^2J_{^{13}C-^{31}P}$ = 11.0, *ortho*-PhP), 131.76 (d, $^4J_{^{13}C-^{31}P}$ = 2.9, *para*-PhP), 150.22 (d, $^1J_{^{13}C-^{31}P}$ = 68.2, PC═N), 151.64 (br. S, NC═N), 156.38, 158.31 (both s, PhC═N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ, ppm: 30.59. $^{19}F\{^1H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: −167.70, −169.50 (both q, $^1J_{^{11}B-^{19}F}$ = 16.8). $^{11}B\{^1H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 3.35, 3.78 (both d, $^1J_{^{11}B-^{19}F}$ = 16.8). IR (KBr) ν/cm^{-1}: 928, 943, 1063, 1108, 1158 ν(N–O), 1213 m ν(B–O) + ν(B–F), 1550sh, 1580 ν(C═N). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} L cm^{-1}): 255(28), 267(0.9), 289(17), 290(2.4), 341(4.2), 394(1.0), 482(10), 489(13), 522(2.2).

$FeBd_2(((C_6H_5)_2P(S))(H_2N(CH_2)_5NH)Gm)(BF)_2$. Complex $FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$ (0.1 g, 0.108 mmol) was dissolved/suspended in acetonitrile (2 ml) and cadaverine (0.11 g, 1.08 mmol) and triethylamine (0.15 ml, 1.08 mmol) were added. The reaction mixture was stirred for 12 h and evaporated to dryness. The solid residue was washed with water (5 ml) and extracted with dichloromethane (10 ml, in two portions). The dichloromethane solution was evaporated to dryness and purified by preparative TLC on silica gel (first eluent: dichloromethane–acetonitrile 1 : 1 mixture, second eluent: acetonitrile). The second elute was evaporated to dryness, washed with hexane and dried *in vacuo*. Yield: 0.097 g (90%). *Anal. Calc.* for $C_{47}H_{43}N_8O_6B_2F_2FePS$ (%): C, 56.77; H, 4.36; N, 11.27. Found (%): C, 56.60; H, 4.55; N, 11.30. MS (MALDI-TOF) *m*/*z* (I, %): 994 (90) $[M]^{+\bullet}$, 1017 (60) $[M + Na^+]^+$, 1033 (100) $[M + K^+]^+$. ^1H NMR (CD_2Cl_2): δ, ppm; *J*, Hz: 1.34, 1.45, 1.53 (all br. s, 6H, $CH_2CH_2CH_2$), 2.42 (br. s, 2H, NH_2), 2.66 (br. s, 2H, CH_2NH_2), 3.76 (q, 2H, CH_2NH, $^3J_{^1H-^1H}$ = 5.8), 7.22–7.50 (m, 20H, Ph(Bd)), 7.50–7.70 (m, 6H, *meta*- + *para*-PhP), 7.92 (dd, 4H, *ortho*-PhP, $^3J_{^1H-^1H}$ = 7.1, $^3J_{^1H-^{31}P}$ = 14.5), 8.38 (m, 1H, NH, $^3J_{^1H-^1H}$ = 6.0). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 23.79, 30.31, 32.42 (all s, $CH_2CH_2CH_2$), 41.51 (s, CH_2NH_2), 45.91 (s, CH_2NH), 127.89, 127.94 (both s, *ortho*-Ph(Bd)), 128.65 (d, $^3J_{^{13}C-^{31}P}$ = 13.9, *meta*-PhP), 128.97, 129.20 (both s, *ipso*-Ph-(Bd)), 130.03 (s, *para*-Ph(Bd)), 130.25, 130.54 (both s, *meta*-Ph-(Bd)), 130.71 (d, $^1J_{^{13}C-^{31}P}$ = 91.7, *ipso*-PhP), 131.58 (d, $^2J_{^{13}C-^{31}P}$ = 12.1, *ortho*-PhP), 132.52 (d, $^4J_{^{13}C-^{31}P}$ = 2.9, *para*-PhP), 143.04 (d, $^1J_{^{13}C-^{31}P}$ = 64.9, PC═N), 152.05 (d, $^2J_{^{13}C-^{31}P}$ = 16.1, NC═N), 155.94, 157.93 (both s, PhC═N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ, ppm: 34.74. $^{19}F\{^1H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: −167.40, −168.90 (both q, $^1J_{^{11}B-^{19}F}$ = 11.0). $^{11}B\{^1H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 3.40, 3.70 (both d, $^1J_{^{11}B-^{19}F}$ = 11.0). IR (KBr) ν/cm^{-1}: 922, 944, 1067, 1110, 1176 ν(N–O), 1211 m ν(B–O) + ν(B–F), 1543, 1580sh ν(C═N), 1604 δ(N–H). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} L cm^{-1}): 256(24), 289(17), 320(5.1), 378(3.4), 429(3.6), 468(6.3), 496(16), 533(6.9).

$[FeBd_2(((C_6H_5)_2P(S))Gm)(BF)_2]_2(NH(CH_2)_5NH)$

Procedure 1. Complex $FeBd_2\{(((C_6H_5)_2P(S))ClGm\}(BF)_2$ (0.2 g, 0.216 mmol) was dissolved/suspended in acetonitrile (5 ml) and cadaverine (0.006 g, 0.058 mmol) and triethylamine (0.016 ml, 0.117 mmol) were added. The reaction mixture was stirred for 24 h and evaporated to dryness. The solid residue was washed with water (5 ml) and extracted with dichloromethane (10 ml, in two portions). The dichloromethane extract was evaporated to dryness and purified by preparative TLC on silica gel (eluent: dichloromethane–acetonitrile 1 : 1 mixture). The major elute was evaporated to dryness, washed with hexane and dried *in vacuo*. Yield: 0.095 g (86%).

Procedure 2. Complex $FeBd_2(((C_6H_5)_2P(S))(H_2N(CH_2)_5NH)Gm)(BF)_2$ (0.05 g, 0.05 mmol) and triethylamine (0.011 ml, 0.076 mmol) were dissolved/suspended in acetonitrile (2 ml) and complex $FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$ (0.07 g, 0.076 mmol) was added. The reaction mixture was stirred for 24 h and evaporated to dryness. The solid clathrochelate product was isolated like in Procedure 1. Yield: 0.085 g (90%). *Anal. Calc.* for $C_{89}H_{72}N_{14}O_{12}B_4F_4Fe_2P_2S_2$ (%): C, 56.66; H, 3.85; N, 10.39. Found (%): C, 56.78; H, 4.04; N, 10.45. MS (MALDI-TOF) *m*/*z* (I, %): 1888 (50) $[M]^{+\bullet}$, 1911 (75) $[M + Na^+]^+$, 1927 (100) $[M + K^+]^+$. ^1H NMR (CD_2Cl_2): δ, ppm; *J*, Hz: 1.30 (pentet, 4H, $CH_2CH_2CH_2CH_2NH$, $^3J_{^1H-^1H}$ = 8.0), 1.45 (pentet, 2H, $CH_2CH_2CH_2NH$, $^3J_{^1H-^1H}$ = 8.0), 3.73 (q, 4H, CH_2NH, $^3J_{^1H-^1H}$ = 5.8),

7.25–7.35 (m, 40H, Ph(Bd)), 7.40–7.55 (m, 12H, *meta*- + *para*-PhP), 7.87 (dd, 8H, *ortho*-PhP, $^{3}J_{^{1}H-^{1}H}$ = 8.0, $^{3}J_{^{1}H-^{31}P}$ = 16.0), 8.36 (m, 2H, NH, $^{3}J_{^{1}H-^{1}H}$ = 5.2). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 23.63 (s, *C*H_2CH$_2$CH$_2$NH), 30.00 (s, H$_2$CH_2*C*H$_2$CH$_2$NH), 45.79 (s, CH_2NH), 127.71, 127.78 (both s, *ortho*-Ph(Bd)), 128.66 (d, $^{3}J_{^{13}C-^{31}P}$ = 13.9, *meta*-PhP), 128.92, 129.21 (both s, *ipso*-Ph(Bd)), 129.79 (s, *para*-Ph(Bd)), 130.45, (s, *meta*-Ph(Bd)), 130.53 (d, $^{1}J_{^{13}C-^{31}P}$ = 91.3, *ipso*-PhP), 130.83 (s, *meta*-Ph(Bd)), 131.64 (d, $^{2}J_{^{13}C-^{31}P}$ = 12.1, *ortho*-PhP), 132.50 (d, $^{4}J_{^{13}C-^{31}P}$ = 2.9, *para*-PhP), 142.68 (d, $^{1}J_{^{13}C-^{31}P}$ = 64.2, PC=N), 151.71 (d, $^{2}J_{^{13}C-^{31}P}$ = 16.9, NC=N), 155.78, 157.72 (both s, PhC=N). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) δ, ppm: 34.67. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: −168.30, −169.20 (both q, $^{1}J_{^{11}B-^{19}F}$ = 12.0). $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 3.53, 3.77 (both d, $^{1}J_{^{11}B-^{19}F}$ = 12.0). IR (KBr) ν/cm^{-1}: 911, 924, 941, 1060, 1111, 1176 ν(N–O), 1212 m ν(B–O) + ν(B–F), 1542, 1580sh ν(C=N), 1602 δ(N–H). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} L cm^{-1}): 260(56), 288(30), 307(16), 356(5.9), 415(8.1), 468(15), 497(39), 548(10).

[Pd(FeBd$_2$(((C$_6$H$_5$)$_2$P(S))(2-NCH$_2$Py)Gm)(BF)$_2$)Cl]. Complex FeBd$_2$(((C$_6$H$_5$)$_2$P(S))(2-NHCH$_2$Py)Gm)(BF)$_2$ (0.138 g, 0.138 mmol) was dissolved in dichloromethane (2 ml) and a solution of Pd(C$_6$H$_5$CN)$_2$Cl$_2$ (0.053 g, 0.138 mmol) in dichloromethane (1 ml) and triethylamine (0.019 ml, 0.138 mmol) were added. The reaction mixture was stirred for 2 h and left overnight. The precipitate formed was filtered off, washed with dichloromethane (2 ml, in two portions) and dried *in vacuo*. Yield: 0.142 g (90%). The product was additionally purified by preparative TLC on silica gel (eluent: dichloromethane–hexane 1 : 1 mixture). The major elute was evaporated to dryness, washed with hexane and dried *in vacuo*. Yield: 0.13 g (84%). *Anal. Calc.* for $C_{48}H_{36}N_8O_6B_2ClF_2FePPdS$ (%): C, 50.52; H, 3.18; N, 9.82; S, 2.81. Found (%): C, 50.53; H, 3.29; N, 9.69; S, 2.66. MS (MALDI-TOF) *m*/*z* (I, %): (positive range) 1105 (100) $[M - Cl^-]^{+\bullet}$, 1141 (75) $[M]^{+\bullet}$, 1164 (15) $[M + Na^+]^+$, 1180 (5) $[M + K^+]^+$; (negative range) – 1141 $[M]^{-\bullet}$. ^{1}H NMR (CD_2Cl_2): δ, ppm; *J*, Hz: 5.14 (s, 2H, CH_2), 7.32–7.47 (m, 20 + 1H, Ph(Bd) + C^{5}H(Py)), 7.54 (dt, 1H, C^{3}H(Py), $^{3}J_{^{1}H-^{1}H}$ = 7.7, $^{4}J_{^{1}H-^{1}H}$ = 1.5), 7.86 (dt, 1H, C^{4}H(Py), $^{3}J_{^{1}H-^{1}H}$ = 7.7, $^{4}J_{^{1}H-^{1}H}$ = 1.5), 7.63–7.80 (m, 6H, *meta*- + *para*-PhP), 8.00 (dd, 4H, *ortho*-PhP, $^{3}J_{^{1}H-^{1}H}$ = 7.2, $^{3}J_{^{1}H-^{31}P}$ = 15.2), 8.92 (d, 1H, C^{6}H(Py), $^{3}J_{^{1}H-^{1}H}$ = 5.0). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 63.36 (s, CH_2N), 119.74 (s, C^3(Py)), 122.61 (s, C^5(Py)), 126.05 (d, $^{1}J_{^{13}C-^{31}P}$ = 89.5, *ipso*-PhP), 127.79, 127.89 (both s, *ortho*-Ph(Bd)), 129.08 (s, *ipso*-Ph(Bd)), 129.13 (d, $^{3}J_{^{13}C-^{31}P}$ = 13.9, *meta*-PhP), 129.31 (s, *ipso*-Ph(Bd)), 129.87, 129.92 (both s, *para*-Ph(Bd)), 130.30, 130.55 (both s, *meta*-Ph(Bd)), 132.34 (d, $^{2}J_{^{13}C-^{31}P}$ = 11.7, *ortho*-PhP), 133.65 (d, $^{4}J_{^{13}C-^{31}P}$ = 2.9, *para*-PhP), 138.98 (s, C^4(Py)), 148.06 (d, $^{1}J_{^{13}C-^{31}P}$ = 74.5, PC=N), 148.18 (s, C^6(Py)), 155.62 (br. s, NC=N), 155.84, 157.97 (both s, PhC=N), 165.21 (s, C^2(Py)). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) δ, ppm: 31.59. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: −166.13, −169.31 (both q, $^{1}J_{^{11}B-^{19}F}$ = 12.5). $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 3.25, 3.57 (both d, $^{1}J_{^{11}B-^{19}F}$ = 12.5). IR (KBr) ν/cm^{-1}: 904 m, 941, 954, 1058, 1109, 1172 ν(N–O), 1205 m ν(B–O) + ν(B–F), 1544, 1574 ν(C=N), 1556 δ(N–H). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} L cm^{-1}): 257(34), 287(17), 331(6.4), 428(5.8), 488(12), 525(7.5), 575(4.4), 605(3.2).

[Pd(FeBd$_2$(((C$_6$H$_5$)$_2$P(S))(2-NCH$_2$CH$_2$Py)Gm)(BF)$_2$)Cl]. This compound was prepared by the same procedure as the complex [Pd(FeBd$_2${((C$_6$H$_5$)$_2$P(S))[2-NCH$_2$Py]Gm}(BF)$_2$)Cl]; Pd(C$_6$H$_5$CN)$_2$Cl$_2$ (0.0465 g, 0.121 mmol) and the complex FeBd$_2${((C$_6$H$_5$)$_2$P(S))[2-NHCH$_2$CH$_2$Py]Gm}(BF)$_2$ (0.123 g, 0.121 mmol) (instead of FeBd$_2${((C$_6$H$_5$)$_2$P(S))[2-NHCH$_2$Py]Gm}(BF)$_2$) were used. Yield: 0.192 g (85%). *Anal. Calc.* for $C_{49}H_{38}N_8O_6B_2ClF_2FePPdS$ (%): C, 50.95; H, 3.32; N, 9.70; S, 2.78. Found (%): C, 51.10; H, 3.41; N, 9.55; S, 2.63. MS (MALDI-TOF) *m*/*z* (I, %): (positive range) 1119 (100) $[M - Cl^-]^{+\bullet}$, 1155 (40) $[M]^{+\bullet}$; (negative range) – 1155 $[M]^{-\bullet}$. ^{1}H NMR (CD_2Cl_2): δ, ppm; *J*, Hz: 3.52 (m, 2H, CH_2Py, $^{3}J_{^{1}H-^{1}H}$ = 6.4), 3.79 (m, 2H, *C*H_2NH, $^{3}J_{^{1}H-^{1}H}$ = 6.4), 7.25–7.44 (m, 20H, Ph(Bd)), 7.54 (m, 1H, C^{4}H(Py), $^{3}J_{^{1}H-^{1}H}$ = 7.8), 7.64–7.83 (m, 6H + 1H, *meta*- + *para*-PhP + C^{3}H(Py)), 7.88 (dt, 1H, C^{5}H(Py), $^{3}J_{^{1}H-^{1}H}$ = 7.6, $^{4}J_{^{1}H-^{1}H}$ = 1.5), 8.02 (dd, 4H, *ortho*-PhP, $^{3}J_{^{1}H-^{1}H}$ = 7.3, $^{3}J_{^{1}H-^{31}P}$ = 15.0), 8.61 (d, 1H, C^{6}H(Py), $^{3}J_{^{1}H-^{1}H}$ = 5.0). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 40.33 (s, CH_2Py), 45.99 (s, CH_2N), 122.46 (s, C^3(Py)), 124.37 (s, C^5(Py)), 126.51 (d, $^{1}J_{^{13}C-^{31}P}$ = 89.5, *ipso*-PhP), 127.76, 127.81 (both s, *ortho*-Ph(Bd)), 128.96 (d, $^{3}J_{^{13}C-^{31}P}$ = 14.3, *meta*-PhP), 129.13, 129.30 (both s, *ipso*-Ph(Bd)), 129.79, 129.83 (both s, *para*-Ph(Bd)), 130.29, 130.47 (both s, *meta*-Ph(Bd)), 132.56 (d, $^{2}J_{^{13}C-^{31}P}$ = 12.1, *ortho*-PhP), 133.47 (d, $^{4}J_{^{13}C-^{31}P}$ = 3.3, *para*-PhP), 139.39 (s, C^4(Py)), 148.55 (d, $^{1}J_{^{13}C-^{31}P}$ = 75.5, PC=N), 151.04 (s, C^6(Py)), 155.49 (d, $^{2}J_{^{13}C-^{31}P}$ = 15.0, NC=N), 155.76, 157.88 (both s, PhC=N), 159.09 (s, C^2(Py)). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) δ, ppm: 31.18. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: −167.07, −168.61 (both q, $^{1}J_{^{11}B-^{19}F}$ = 15.0). $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2) δ, ppm; *J*, Hz: 3.30, 3.42 (both d, $^{1}J_{^{11}B-^{19}F}$ = 15.0). IR (KBr) ν/cm^{-1}: 910 m, 923, 941 m, 1000, 1058, 1111, 1159, 1173 ν(N–O), 1209 m ν(B–O) + ν(B–F), 1544 m ν(C=N) + δ(N–H), 1580sh ν(C=N). UV-vis (CH_2Cl_2): λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} L cm^{-1}): 237(51), 271(2.4), 298(3.9), 326(6.6), 386(3.0), 415(2.2), 438(0.7), 488(13), 577(6.4).

X-ray crystallography

Single crystals of the clathrochelates FeBd$_2$(((C$_6$H$_5$)$_2$P(S))ClGm)(BF)$_2$·CH_2Cl_2, FeBd$_2$(((C$_6$H$_5$)$_2$P(S))(*n*-C$_4$H$_9$NH)Gm)(BF)$_2$·2 CH_2Cl_2, FeBd$_2$(((C$_6$H$_5$)$_2$P(S))(2-NHCH$_2$Py)Gm)(BF)$_2$·C$_4$H$_{10}$O·CH_2Cl_2, FeBd$_2$(((C$_6$H$_5$)$_2$P(S))(CH$_3$SCH$_2$CH$_2$NCH$_3$)Gm)(BF)$_2$·2 $CHCl_3$ and [FeBd$_2$(((C$_6$H$_5$)$_2$P(S))Gm)(BF)$_2$]$_2$(NH(CH$_2$)$_5$NH)·3.5 CH_2Cl_2 and two palladium(II) complexes [Pd(FeBd$_2$(((C$_6$H$_5$)$_2$P(S))(2-NCH$_2$Py)Gm)(BF)$_2$)Cl]·CH_2Cl_2·H$_2$O and [Pd(FeBd$_2$(((C$_6$H$_5$)$_2$P(S))(2-NCH$_2$CH$_2$Py)Gm)(BF)$_2$)Cl]·2 CH_2Cl_2 with N,S-donor macrobicyclic ligands were grown from their saturated solutions in dichloromethane–hexane, chloroform–heptane, diethyl ether–dichloromethane and diethyl ether–hexane mixtures at room temperature. The intensities of reflections were measured at 100(2) K with a Bruker Apex II DUO diffractometer using Cu-Kα radiation for FeBd$_2$(((C$_6$H$_5$)$_2$P(S))(2-NHCH$_2$Py)Gm)(BF)$_2$ (λ = 1.54178 Å, microfocus tube with multilayer optics) and Mo-Kα radiation for the other X-rayed cage compounds (λ = 0.71073 Å, graphite monochromator). Absorption corrections were performed with the SADABS program,[20] using multipole measurements of equivalent reflections. The structures were solved by the direct method and refined by full-matrix least squares method against F^2 of all data, using SHELXTL PLUS software[21]

and OLEX2 program.[22] Non-hydrogen atoms were found on difference Fourier maps and refined with anisotropic displacement parameters with an exception of disordered ones. A methyl moiety of methylsulfide group, one phenyl ring and a solvate chloroform molecule in the crystal of $FeBd_2(((C_6H_5)_2P(S))(CH_3SCH_2CH_2NCH_3)Gm)(BF)_2\cdot 2CHCl_3$ are disordered over two parts with 0.75 : 0.25 (for carbon and hydrogen atoms) or 0.5 : 0.5 (for chlorine atoms) site occupancies and were refined in isotropic approximation for carbon atoms. The unit cells of the crystal of clathrochelates $FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2Py)Gm)(BF)_2$ and $[FeBd_2(((C_6H_5)_2P(S))Gm)(BF)_2]_2(NH(CH_2)_5NH)$ contain 2 and 3.5 highly disordered solvate dichloromethane molecules, respectively, which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[23] The chemical formula, formula weight and D_{calc} were calculated taking these solvate molecules into account. In order to avoid strong anisotropy of some atoms in the molecules $FeBd_2(((C_6H_5)_2P(S))(n\text{-}C_4H_9NH)Gm)(BF)_2$, $[Pd(FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2Py)Gm)(BF)_2)Cl]$ and $[Pd(FeBd_2(((C_6H_5)_2P(S))(2\text{-}NCH_2CH_2Py)Gm)(BF)_2)Cl]$, ISOR command was applied. Besides, in the latter case SADI command was used for the refinement of the solvate dichloromethane molecules, which are disordered over two sites. The positions of hydrogen atoms were calculated and included in the refinement in isotropic approximation by the riding model with the $U_{iso}(H) = 1.2U_{eq}(C)$, where $U_{eq}(C)$ are equivalent thermal parameters of parent atoms.

The main crystallographic and refinement parameters are listed in Tables S1 and S2 (see the ESI¶).

Catalytic experiments

General procedure. An aryl halide (0.5 mmol), phenylboronic acid (0.079 g, 0.65 mmol), K_3PO_4 (0.159 g, 0.75 mmol) and a palladium-containing clathrochelate catalyst (0.005 mmol) were dissolved/suspended in DMF (15 ml) under argon and the stirred reaction mixture was heated at 100 °C for 4 h. Then, the reaction mixture was cooled to r.t. and water (3 ml) was added. The organic products were extracted with benzene (10 ml), the extract was dried with Na_2SO_4 and then analyzed by a GC method.

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