Electronic Supporting Information

for

Clathrochelates meet phosphorus. New thio- and phosphorylation reactions of an iron(II) dichloroclathrochelate precursor and preparation of its first phosphorus(III)-containing macrobicyclic derivative

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General considerations

The reagents used, $FeCl_2 \cdot 4H_2O$, α-benzildioxime (denoted as H_2Bd), $BF_3 \cdot O(C_2H_5)_2$, diphenylphosphine oxide, triethylbenzylammonium chloride, diethyl thiophosphite, 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. [S1]. The dichloroclathrochelate precursor $FeBd_2(Cl_2Gm)(BF)_2$ was obtained as described elsewhere.[3a]

Analytical data (C, H, N contents) were obtained with a Carlo Erba model 1106 microanalyzer.

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 reflecto-mol mode. The ionization was induced by UV-laser with wavelength 336 nm. The sample was applied to a nickel plate, 2,5-dihydroxybenzoic acid was used as a matrix. The accuracy of 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.

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

Supporting Information References

S1. G.Ponzio, F.Baldrocco, *Gazz. Chim.Ital.*, 1930, **60**, 415–420.

Table S1 Maxima {λ_{max}, nm ($\varepsilon \cdot 10^{-3}$, mol^{-1} l cm^{-1})} of the UV–vis spectra for the mono- and diphosphorylated iron(II) mono- and bis-clathrochelates and their dichloroclathrochelate precursor

Complex	λ_1 (ε_1)	λ_2 (ε_2)	λ_3 (ε_3)	λ_4 (ε_4)	λ_5 (ε_5)	λ_6 (ε_6)	λ_7 (ε_7)	λ_8 (ε_8)	λ_9 (ε_9)
$FeBd_2(Cl_2Gm)(BF)_2$ [3a]	264 (14)	285 (7.7)		311 (3.6)	399 (3.2)	448 (3.5)	470 (19)		
$FeBd_2(((C_6H_5)_2P(O))ClGm)(BF)_2$	266(20)	298(6.9)		336(2.9)	391(3.1)	426(3.9)	452(8.8)	479(12)	507(5.9)
$FeBd_2(((C_2H_5O)_2P(S))ClGm)(BF)_2$	268(23)	287(4.2)	303(6.1)	318(5.0)	378(3.6)	432(3.9)	467(19)	495(11)	
$FeBd_2(((C_2H_5O)_2P(S))_2Gm)(BF)_2$	271(13)	291(13)				433(6.4)	468(20)		506(5.6)
$FeBd_2(((C_6H_5)_2P(S))ClGm)(BF)_2$ [1]	262(33)	299(11)		355(4.0)	412(4.4)	441(7.7)	467(19)	499(15)	514(2.9)
$FeBd_2(((C_6H_5)_2P(S))(n\text{-}C_4H_9NH)Gm)(BF)_2$ [1]	256(23)	283(15)	300(11)	356(3.4)	414(3.9)		465(8.2)	496(20)	542(6.6)
$FeBd_2(((C_6H_5)_2P(S))(H_2N(CH_2)_5NH)Gm)(BF)_2$ [1]	256(24)	289(17)		320(5.1)	378(3.4)	429(3.6)	468(6.3)	496(16)	533(6.9)
$FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2Py)Gm)(BF)_2$ [[1]	256(18)	284(16)		320(3.3)	407(3.1)		469(5.0)	496(12)	533(4.3)
$FeBd_2(((C_6H_5)_2P(S))(2\text{-}NHCH_2CH_2Py)Gm)(BF)_2$ [1]	250(14)	267(3.6)	277(20)	299(4.8)	406(2.7)			490(20)	543(4.6)
$FeBd_2(((C_6H_5)_2P(S))(CH_3SCH_2CH_2NCH_3)Gm)(BF)_2$ [1]	255(28)	267(0.9)	289(17)	290(2.4)	341(4.2)	394(1.0)	482(10)	489(13)	522(2.2)
$[FeBd_2(((C_6H_5)_2P(S))Gm)(BF)_2]_2(NH(CH_2)_5NH)$ [1]	260(56)	288(30)	307(16)	356(5.9)	415(8.1)		468(15)	497(39)	548(10)

Table S2. Crystallographic data and refinement parameters for the complexes $FeBd_2(((C_6H_5)_2P(O))ClGm)(BF)_2 \cdot 0.5\ O(C_2H_5)_2$, $FeBd_2(((C_2H_5O)_2P(S)))ClGm)(BF)_2 \cdot 2\ CH_2Cl_2$, $FeBd_2(((C_2H_5O)_2P(S))_2Gm)(BF)_2 \cdot 1.75\ C_6H_{14}$ and $FeBd_2(((C_6H_5)_2P)ClGm)(BF)_2 \cdot 3CH_2Cl_2$

	$FeBd_2(((C_6H_5)_2P(O))ClGm)(BF)_2 \cdot$ 0.5 $(C_2H_5)_2O$	$FeBd_2(((C_2H_5O)_2P(S)))ClGm)(BF)_2 \cdot$ 2 CH_2Cl_2	$FeBd_2(((C_2H_5O)_2P(S))_2Gm)(BF)_2 \cdot$ 1.75 C_6H_{14}	$FeBd_2(((C_6H_5)_2P)ClGm)(BF)_2 \cdot$ $3CH_2Cl_2$
Empirical formula	$C_{44}H_{35}B_2ClF_2FeN_6O_{7.5}P$	$C_{36}H_{34}B_2Cl_5F_2FeN_6O_8PS$	$C_{48.5}H_{64.5}B_2F_2FeN_6O_{10}P_2S_2$	$C_{45}H_{36}B_2Cl_7F_2FeN_6O_6P$
Fw	949.67	1034.44	1133.09	1151.39
Color, habit	brownish-red, prism	pale-brown, plate	red, prism	red, plate
Crystal size (mm^3)	0.35×0.32×0.21	0.28 × 0.15 ×0 .04	0.32 × 0.29 × 0.09	0.26 × 0.12 × 0.04
Temperature, K	100.0(2)	100.0(2)	120.0(2)	120.0(2)
a (Å)	12.320(1)	15.441 (2)	38.597(2)	16.4722(3)
b (Å)	13.773(2)	16.407 (2)	38.597 (2)	12.3493(2)
c (Å)	13.832(2)	17.367 (2)	23.994 (2)	30.3441(6)
	116.261(3)	90	90	90
β (°)	91.671 (3)	90	90	126.470(1)
	95.321(3)	90	120	90
V (Å^3)	2089.3(4)	4399.8 (10)	30955 (3)	4963.81(16)
Z	2	4	18	4
Crystal system	triclinic	orthorhombic	hexagonal	monoclinic
Space group	$P\bar{1}$	P 2_1 2_1 2_1	R $\bar{3}$	P 2_1/c
d_{calc} (g·cm^{-3})	1.510	1.556	1.094	1.541
μ (mm^{-1})	0.534	0.792	3.213	6.734
Independent reflections (R_{int})	11049 (0.030)	8621 (0.111)	12025 (0.050)	8717 (0.1501)
Obs.refl./restraints/ parameters	8961 / 0 / 580	5649 / 17 / 483	9865 / 3 / 605	6464 / 0 / 631
R,[a] % [I > 2σ(I)]	0.043	0.094	0.064	0.041
R_w,[b] %	0.094	0.193	0.182	0.092
GOF[c]	1.05	1.05	1.10	1.00
F(000)	974	2104	10683	2336

[a]$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$R_w = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2))]^{1/2}$. [c]$GOF = [\Sigma w(F_o^2-F_c^2)^2/(N_{obs}-N_{param})]^{1/2}$