Electronic Supplementary Material (ESI) for ChemComm.

Selective Conversion of Glycerol to Lactic Acid with Iron Pincer Precatalysts

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- Supporting Information -

CONTENTS

1. Experimental procedures

General. Organic solvents were dried by passing over activated alumina with dry N_2. All solvents were deoxygenated by purging with dry N_2 or using the freeze-pump thaw method. All chemicals were purchased from commercial suppliers and used as received. NMR spectra were recorded on Agilent DD2-400, -500, -600 or Bruker AMX-500 spectrometers at ambient probe temperatures. Chemical shifts are reported with respect to residual internal protio solvent for ^1H and $^{13}C\{^1H\}$ NMR spectra. Compounds **1-6**[1] and **7**[2] were synthesized according to previously reported procedures. All catalytic experiments were performed under an N_2 or Ar atmosphere.

Glycerol conversion to LA. A reactor vial (Radleys, Carousel 12 Place Reaction Station, RR98030) was charged with catalyst (1.5 μmol, 0.02 mol %), glycerol (0.5 mL), co-solvent (1.0 mL) and NaOH (274 mg). Accurate weighing of the precatalyst was facilitated by adding an aliquot of a stock solution of precatalyst in THF and then removing the THF in vacuo prior to addition of other reagents. The vial was connected to a nitrogen line and heated for 3 - 24 h. Upon cooling, water (1 mL), D_2O (1 mL) and sodium(3-trimethylsilylpropionate)2,2,3,3-d_4 (10 mg, internal standard) were added. The yield was calculated by ^1H NMR integration versus the internal standard. The reaction products sodium lactate and formic acid were identified by spiking with authentic samples. Additionally, sodium-4-N-methylaminobutanoate was identified by spiking with an authentic sample. The identity of the other side product was assigned as diglycerols or other glycerol etherification products using ^1H NMR spectroscopy. Based on ^1H NMR analysis, this product is formed regardless of the co-solvent, even upon heating neat glycerol at 140 °C in the presence of base. Glycerol etherification reactions giving diglycerols and higher oligomers have been reported under similar conditions.[3] The NMR spectrum of the species resembles the spectrum of authentic linear diglycerol, although spiking did not give complete overlap, suggesting that the species is either a different isomer or a cyclic or higher oligomer.

General procedure for TH of acetophenone.

To a 1 dram vial equipped with a stir bar were added KOH (11 – 110 mg), **1** (5 μ mol, 2.5 mol %), co-solvent (0.4 mL), glycerol (0.4 mL), and acetophenone (0.2 mmol, 23.3 μL) under an N_2 atmosphere. The vial was capped and heated at 120 ˚C with stirring using a hot plate with a heating block. After 22 h, the reaction was cooled to room temperature and D_2O (1 mL) and sodium(3-trimethylsilylpropionate)2,2,3,3-d_4 (5 mg, internal standard) were added. The yield was calculated by comparing the integration of the product versus the internal standard using ^1H NMR spectroscopy.

Sequential addition reaction.

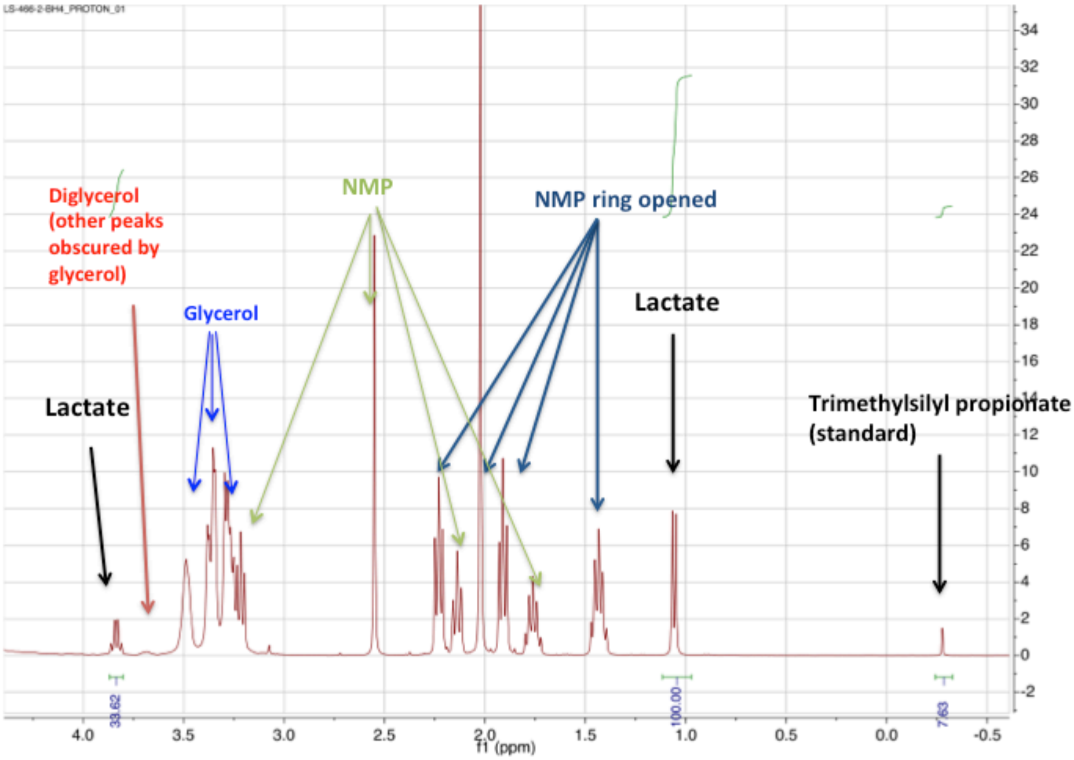
To a reactor vial was added **1** (0.63 mg, 1.5 μmol), glycerol (0.5 mL), NMP (0.5 mL) and NaOH (274 mg). The vial was heated under N_2 at 140 ˚C. After each hour, 0.63 mg of **1** was added as a stock solution in NMP (30 μL of solution, added 5 times total). For the corresponding control reaction without sequential addition, 6.3 mg **1** was added initially and each hour 30 μL of NMP was added. After 6 hours, the reactions were stopped and worked up as described above.

Large scale synthesis of compound 7

7 was initially prepared by forming 4-N-methylaminobutanoaic acid according to reported procedure[2] (heating NMP with stoichiometric $Ba(OH)_2$ in water and neutralizing) and subsequently forming the sodium salt by deprotonation with stoichiometric NaOH. For preparation of larger amounts of **7**, we used a modified procedure in which NaOH is substituted for $Ba(OH)_2$ in the synthesis: 5 mL NMP, 2.07 mg NaOH (1 eq.) and 5 mL H_2O were heated in a round bottom flask at 110 ˚C for 6 h. The solvent was removed in vacuo and the solid washed with ether. The identity of the solid product was confirmed by ^1H NMR by spiking with a sample prepared by deprotonating authentic 4-N-methylaminobutanoaic acid with NaOH.

2. ^{1}H NMR spectra

Figure S1. Reaction products from catalytic reaction with **1**.



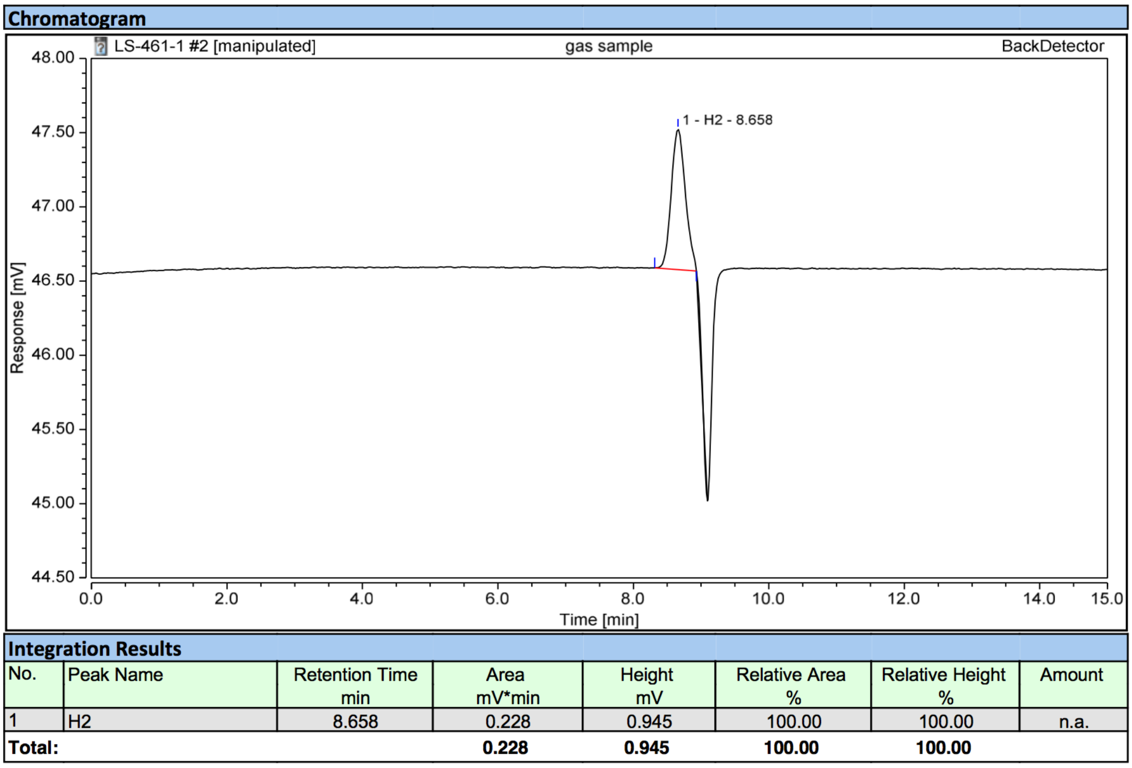
3. Gas burette monitoring of reaction progress and GC analysis

The reaction progress was monitored by gas burette using our previously reported setup.[4] To a Schlenk tube was added 1.5 μmol catalyst, 0.5 mL each of glycerol, NMP and water, and 274 mg NaOH. The tube was then coupled to a condenser attached to our gas burette setup and heated at 140 °C. The gas measurements were corrected by subtracting measurements taken on a blank sample. After completion of the reaction, the total volume of produced gas was converted to moles using the ideal gas law with T = 298 K. The amount of H_2 produced was in excellent agreement with the amount of LA in the reaction mixture as quantified by ^1H NMR spectroscopy (>95 % agreement between the two values).

GC identification of H_2

The gas collected in the gas burette from a catalytic run with complex **1** was analyzed using a gas chromatograph. *[Specifications: Thermo Scientific Trace 1300 GC with mol sieve 5Å PLOT capillary GC column (30 m length, 0.53 mm inner diameter, 30 μm average thickness) purchased from Sigma-Aldrich; 0.95 mL/min flow of N2 carrier gas; Oven: 35 °C; TCD detector, negative polarity, 150 °C filament, 1 mL/min reference gas.]* After completion of a burette reaction, a sealed evacuated Schlenk flask equipped with a rubber septum was attached to tubing leading to the burette 3-way stopcock. The stopcocks on the Schlenk flask and burette were then opened, allowing gas to flow from the burette into the flask. A 30 μL gas sample for GC analysis was then taken from the flask using a gas-tight syringe. The resulting chromatogram (Figure S2) shows two peaks, which were identified as H_2 (retention time = 8.658 min.) and Ar (used as atmosphere for the reaction) based on comparison of retention time with authentic samples.

Figure S2. Chromatogram of gas produced during catalysis with **1**.



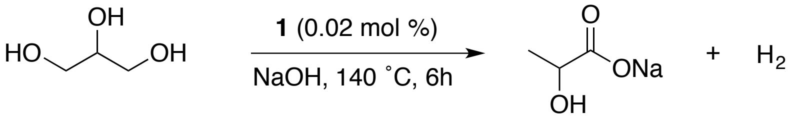
Chromatogram

Integration Results

No.	Peak Name	Retention Time min	Area mV*min	Height mV	Relative Area %	Relative Height %	Amount
1	H2	8.658	0.228	0.945	100.00	100.00	n.a.
Total:			**0.228**	**0.945**	**100.00**	**100.00**	

4. Additional catalysis experiments

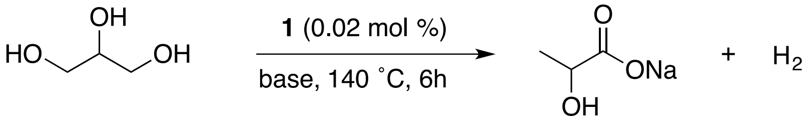
Table S1: Solvent screen using complex **1**.



Entry	Co-solvent	TON	% yield LA
1	DMPU/water	66	2
2	DMPU/water with **7** (200 eq. vs. catalyst)	58	2
3	**7**/water	730	16
4	NMP/water with 200 eq. sodium lactate[a]	760	17
5	N-methylpyridone/water	43	1
6	1,3 Dimethoxybenzene/water	8	<1
7	t-Butanol/water	<1	<1
8	2-methyl-1-phenyl-2-propanol/water	11	<1
9	Sulfolane/water	55	1
10	Pyridine/water	16	<1
11	Phenol/water	11	<1
12	IL[b]/water	130	3

All rxns run with **1** (0.02 mol %) and 1:1:1 glycerol:water:solvent with 1 eq. NaOH *vs*. glycerol at 140 ˚C for 6 h. [a]Lactate added to test for product inhibition of catalysis [b]IL = 1,2,3 trimethylimidazolium methyl sulfate.

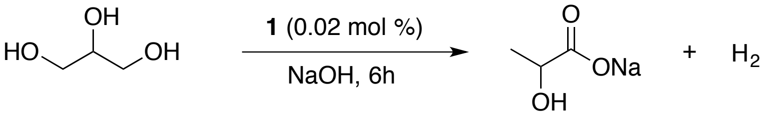
Table S2: Base screen using complex **1**.



Entry	Base	eq. vs. glycerol	TON
1	NaOH	1	770
2	NaOH	1.5	670
3	NaOH	0.5	450
4	KOH	1	610
5	NaOAc	1	<5
6	K_2CO_3	1	<5
7	None	0	<5

All rxns run with catalyst (0.02 mol %) and 1:1:1 glycerol:water:NMP at 140 ˚C for 6 h.

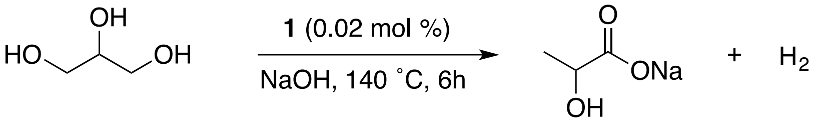
Table S3: Temperature screen using complex **1**.



Entry	Temperature	TON
1	115	400
2	140	770
3	160	130

All rxns run with catalyst (0.02 mol %) and 1:1:1 glycerol:water:NMP with 1 eq. base *vs*. glycerol for 6 h.

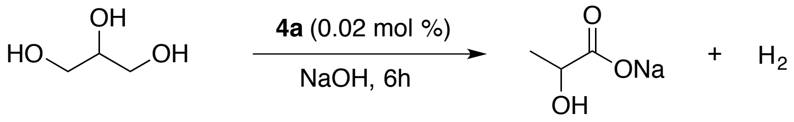
Table S4: Optimization of co-solvent ratio using complex **1**.



Entry	NMP/water ratio	TON
1	2:1	360
2	1:1	770
3	1:2	650

All rxns run with catalyst (0.02 mol %), 0.5 mL glycerol and 1 mL NMP/water co-solvent with 1 eq. base *vs*. glycerol for 6 h.

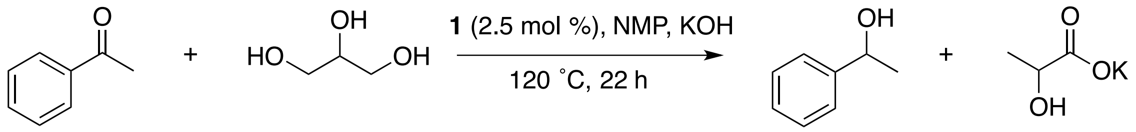
Table S5: Solvent screen using complex **4a**.



Entry	Loading (%)	Solvent	Additive[a]	[glycerol] (M)	Temp.(˚C)	TON	% yield
1	0.1	Dimethylacetamide	KOH	4.0	115	4	2
2	0.1	DMF	KOH	4.0	115	3	1
3	0.02	Dimethoxybenzene /water (1:1)	NaOH	4.6	140	8	<1
4	0.5	THF	-	0.2	85	-	-
5	0.5	THF/water (1:1)	KOH	0.2	85	18	9
6	0.5	ACN	-	0.2	85	4	2
7	0.5	EtOAc	-	0.2	85	8	4
8[c]	0.5	EtOAc	NaOAc	0.2	85	8	4
9[c]	0.5	EtOAc	K_2CO_3	0.2	85	<5	<3
10	0.5	Toluene	-	0.2	85	10	5
11	0.5	Toluene	NEt_3, $LiBF_4$[b]	0.2	115	10	5
12	0.5	Toluene	K_2CO_3	0.2	115	9	5

All rxns run with catalyst (3 or 6 μmol) and glycerol for 24 h. [a]1 eq. base vs. glycerol added unless stated otherwise. [b]100 eq. $LiBF_4$ *vs*. catalyst. [c]>50 % glycerol converted into a mixture of glycerol acetate esters. This process occurs with or without catalyst.

Table S6: TH of acetophenone using **1** in dioxane.



Entry	Co-solvent	Catalyst	Eq. KOH vs. substrate	Yield (%)
1	Dioxane	1	1	23
2	Dioxane	1	5	64
3	Dioxane	1	10	55

Experiments run for 22 h at 120 ˚C with **1** (2.5 mol %), glycerol (0.4 mL), co-solvent (0.4 mL) and KOH. [a]Yield calculated based on yield of 1-phenylethanol using ^1H NMR integration with sodium(3-trimethylsilylpropionate)2,2,3,3-d_4 as internal standard.

5. Crystallographic data for complex 2

Experimental

Yellow crystalline blocks of **2** suitable for diffraction were grown from a saturated pentane solution of **2** at -30 ˚C.

Crystallographic details

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structures of **2**. The structure was solved using SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[5] All non-hydrogen atoms were refined anisotropically. Unless otherwise noted, hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The only exceptions are hydrogen atoms H1 and H, which are freely refining. The refined hydrogen bond interaction between H1 and N3 can be found in Table S12. The full numbering scheme of compound **2** is given in Figure S3. Full details of the X-ray structure determination are in the included CIF file. The structure is deposited in the Cambridge Crystallographic Data Centre (CCDC) (Deposition number: CCDC 1418827).

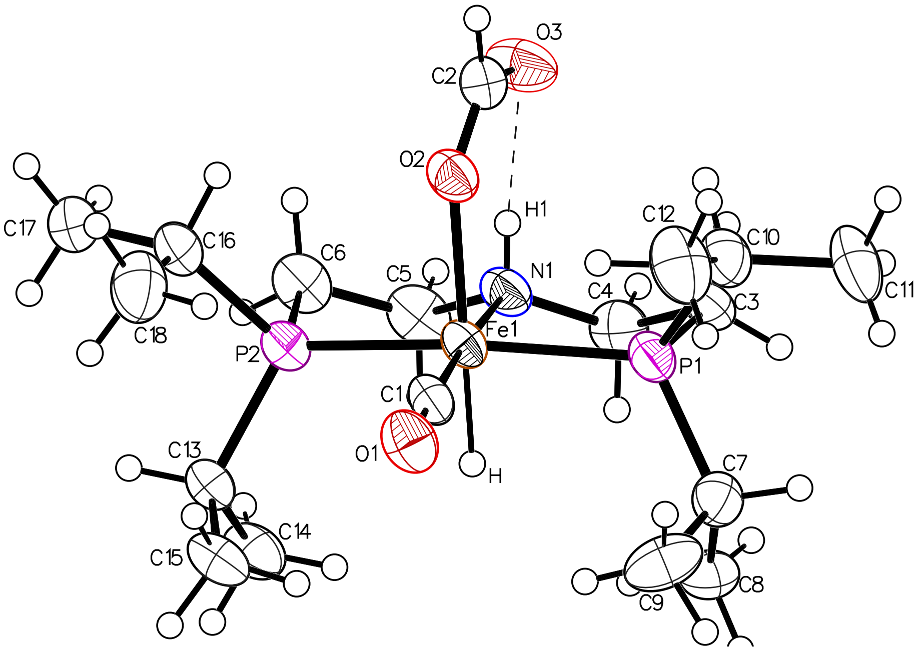


Figure S3. The full numbering scheme of **2**. All atoms shown are depicted with 50% thermal contours. The hydrogen atoms are shown as spheres.

Table S7: Crystal data and structure refinement for compound **2**.

Empirical formula	$C_{18}H_{39}FeNO_3P_2$	
Formula weight	435.29	
Temperature	566(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.8949(7) Å	α = 90°.
	b = 17.1226(12) Å	β = 105.661(3)°.
	c = 13.9266(10) Å	γ = 90°.
Volume	2271.9(3) Å^3	
Z	4	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	6.776 mm^{-1}	
F(000)	936	
Crystal size	0.080 x 0.030 x 0.020 mm^3	
Crystal color and habit	Orange Plate	
Diffractometer	Rigaku Saturn 944+ CCD	
Θ range for data collection	4.187 to 66.594°.	
Index ranges	$-11 \leq h \leq 11$, $-19 \leq k \leq 18$, $-16 \leq l \leq 16$	
Reflections collected	58788	
Independent reflections	3998 [R(int) = 0.1701]	
Observed reflections ($I > 2\sigma(I)$)	2889	
Completeness to θ = 66.594°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.876 and 0.521	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	3998 / 0 / 242	

Goodness-of-fit on F^2	1.023
Final R indices [$I>2\sigma(I)$]	R1 = 0.0596, wR2 = 0.1350
R indices (all data)	R1 = 0.0907, wR2 = 0.1548
Largest diff. peak and hole	0.597 and -0.574 e.Å^{-3}

Table S8: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	4274(1)	7112(1)	6512(1)	31(1)
P(1)	5331(1)	8053(1)	5910(1)	36(1)
P(2)	2842(1)	6186(1)	6755(1)	35(1)
O(1)	6834(3)	6279(2)	7458(2)	46(1)
O(2)	4235(3)	7708(2)	7802(2)	40(1)
O(3)	2563(3)	8623(2)	7343(2)	55(1)
N(1)	2450(4)	7655(2)	5695(3)	37(1)
C(1)	5786(4)	6621(2)	7089(3)	35(1)
C(2)	3533(5)	8286(2)	7942(3)	40(1)
C(3)	3866(5)	8657(2)	5182(3)	43(1)
C(4)	2584(4)	8136(3)	4854(3)	43(1)
C(5)	1208(4)	7144(3)	5359(4)	46(1)
C(6)	1107(4)	6621(3)	6208(4)	45(1)
C(7)	6358(4)	7804(3)	5027(3)	41(1)
C(8)	5430(5)	7511(3)	4027(3)	44(1)
C(9)	7467(5)	7187(3)	5456(4)	59(1)
C(10)	6358(5)	8792(2)	6769(3)	45(1)
C(11)	6884(5)	9473(3)	6259(4)	61(2)
C(12)	7513(5)	8447(3)	7582(4)	62(2)
C(13)	2832(4)	5219(2)	6151(3)	39(1)
C(14)	2119(5)	5246(3)	5033(3)	51(1)
C(15)	4300(4)	4890(3)	6331(4)	49(1)
C(16)	2750(5)	5970(3)	8033(3)	46(1)
C(17)	1392(5)	5556(3)	8093(4)	51(1)

C(18)	4019(5)	5527(3)	8649(4)	60(1)

Table S9: Bond lengths [Å] and angles [°] for **2**.

Fe(1)-C(1)	1.715(4)
Fe(1)-O(2)	2.076(3)
Fe(1)-N(1)	2.076(3)
Fe(1)-P(1)	2.2066(12)
Fe(1)-P(2)	2.2121(12)
Fe(1)-H	1.49(4)
P(1)-C(3)	1.845(4)
P(1)-C(7)	1.845(5)
P(1)-C(10)	1.846(4)
P(2)-C(6)	1.837(4)
P(2)-C(16)	1.845(5)
P(2)-C(13)	1.856(4)
O(1)-C(1)	1.181(4)
O(2)-C(2)	1.253(5)
O(3)-C(2)	1.232(5)
N(1)-C(4)	1.467(6)
N(1)-C(5)	1.478(5)
N(1)-H(1)	0.81(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.517(6)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.508(6)

C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-C(9)	1.525(6)
C(7)-C(8)	1.531(6)
C(7)-H(7)	0.9800
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-C(12)	1.496(6)
C(10)-C(11)	1.529(6)
C(10)-H(10)	0.9800
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-C(15)	1.515(6)
C(13)-C(14)	1.526(6)
C(13)-H(13)	0.9800
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-H(15A)	0.9600

C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-C(18)	1.519(7)
C(16)-C(17)	1.541(6)
C(16)-H(16)	0.9800
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(1)-Fe(1)-O(2)	93.09(16)
C(1)-Fe(1)-N(1)	174.79(18)
O(2)-Fe(1)-N(1)	92.12(14)
C(1)-Fe(1)-P(1)	95.35(14)
O(2)-Fe(1)-P(1)	95.19(9)
N(1)-Fe(1)-P(1)	83.98(11)
C(1)-Fe(1)-P(2)	95.24(14)
O(2)-Fe(1)-P(2)	93.36(9)
N(1)-Fe(1)-P(2)	84.65(11)
P(1)-Fe(1)-P(2)	166.00(5)
C(1)-Fe(1)-H	89.0(15)
O(2)-Fe(1)-H	177.9(15)
N(1)-Fe(1)-H	85.8(15)
P(1)-Fe(1)-H	84.9(16)
P(2)-Fe(1)-H	86.2(16)
C(3)-P(1)-C(7)	104.8(2)
C(3)-P(1)-C(10)	100.7(2)

C(7)-P(1)-C(10)	106.5(2)
C(3)-P(1)-Fe(1)	103.64(15)
C(7)-P(1)-Fe(1)	119.16(15)
C(10)-P(1)-Fe(1)	119.25(15)
C(6)-P(2)-C(16)	101.4(2)
C(6)-P(2)-C(13)	106.5(2)
C(16)-P(2)-C(13)	105.2(2)
C(6)-P(2)-Fe(1)	102.24(15)
C(16)-P(2)-Fe(1)	119.44(14)
C(13)-P(2)-Fe(1)	119.71(15)
C(2)-O(2)-Fe(1)	131.6(3)
C(4)-N(1)-C(5)	109.0(3)
C(4)-N(1)-Fe(1)	115.9(3)
C(5)-N(1)-Fe(1)	115.7(3)
C(4)-N(1)-H(1)	108(3)
C(5)-N(1)-H(1)	106(3)
Fe(1)-N(1)-H(1)	101(3)
O(1)-C(1)-Fe(1)	177.9(4)
O(3)-C(2)-O(2)	128.8(4)
O(3)-C(2)-H(2)	115.6
O(2)-C(2)-H(2)	115.6
C(4)-C(3)-P(1)	107.8(3)
C(4)-C(3)-H(3A)	110.2
P(1)-C(3)-H(3A)	110.2
C(4)-C(3)-H(3B)	110.2
P(1)-C(3)-H(3B)	110.2
H(3A)-C(3)-H(3B)	108.5
N(1)-C(4)-C(3)	109.8(3)
N(1)-C(4)-H(4A)	109.7

C(3)-C(4)-H(4A)	109.7
N(1)-C(4)-H(4B)	109.7
C(3)-C(4)-H(4B)	109.7
H(4A)-C(4)-H(4B)	108.2
N(1)-C(5)-C(6)	109.2(3)
N(1)-C(5)-H(5A)	109.8
C(6)-C(5)-H(5A)	109.8
N(1)-C(5)-H(5B)	109.8
C(6)-C(5)-H(5B)	109.8
H(5A)-C(5)-H(5B)	108.3
C(5)-C(6)-P(2)	108.2(3)
C(5)-C(6)-H(6A)	110.0
P(2)-C(6)-H(6A)	110.0
C(5)-C(6)-H(6B)	110.0
P(2)-C(6)-H(6B)	110.0
H(6A)-C(6)-H(6B)	108.4
C(9)-C(7)-C(8)	108.7(4)
C(9)-C(7)-P(1)	111.5(3)
C(8)-C(7)-P(1)	112.3(3)
C(9)-C(7)-H(7)	108.1
C(8)-C(7)-H(7)	108.1
P(1)-C(7)-H(7)	108.1
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5

C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(12)-C(10)-C(11)	111.5(4)
C(12)-C(10)-P(1)	113.2(3)
C(11)-C(10)-P(1)	114.7(3)
C(12)-C(10)-H(10)	105.5
C(11)-C(10)-H(10)	105.5
P(1)-C(10)-H(10)	105.5
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(15)-C(13)-C(14)	109.8(4)
C(15)-C(13)-P(2)	111.7(3)
C(14)-C(13)-P(2)	112.3(3)
C(15)-C(13)-H(13)	107.6
C(14)-C(13)-H(13)	107.6
P(2)-C(13)-H(13)	107.6

C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(18)-C(16)-C(17)	109.9(4)
C(18)-C(16)-P(2)	113.4(3)
C(17)-C(16)-P(2)	114.5(3)
C(18)-C(16)-H(16)	106.1
C(17)-C(16)-H(16)	106.1
P(2)-C(16)-H(16)	106.1
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5

H(18B)-C(18)-H(18C) 109.5

Table S10: Anisotropic displacement parameters (Å^2 x 10^3) for **2**. The anisotropic displacement factor exponent takes the form: -2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	32(1)	24(1)	34(1)	2(1)	5(1)	3(1)
P(1)	45(1)	27(1)	34(1)	-1(1)	8(1)	-3(1)
P(2)	36(1)	29(1)	39(1)	-2(1)	8(1)	-1(1)
O(1)	41(2)	38(2)	54(2)	8(2)	4(2)	8(1)
O(2)	48(2)	30(2)	38(2)	2(1)	8(1)	4(1)
O(3)	63(2)	49(2)	49(2)	-4(2)	7(2)	21(2)
N(1)	47(2)	27(2)	37(2)	1(2)	9(2)	6(2)
C(1)	41(3)	24(2)	40(3)	0(2)	10(2)	-2(2)
C(2)	49(3)	32(2)	42(3)	3(2)	17(2)	-1(2)
C(3)	63(3)	27(2)	41(3)	1(2)	18(2)	7(2)
C(4)	43(3)	44(3)	39(3)	6(2)	5(2)	12(2)
C(5)	30(2)	45(3)	55(3)	-3(2)	-2(2)	5(2)
C(6)	35(2)	42(3)	56(3)	-2(2)	6(2)	1(2)
C(7)	45(3)	41(3)	37(3)	-3(2)	10(2)	-9(2)
C(8)	50(3)	48(3)	36(3)	-9(2)	12(2)	-1(2)
C(9)	40(3)	92(4)	48(3)	-8(3)	15(2)	10(3)
C(10)	55(3)	38(3)	41(3)	-2(2)	9(2)	-9(2)
C(11)	77(4)	38(3)	57(3)	5(2)	-1(3)	-21(2)
C(12)	60(3)	56(3)	55(3)	1(3)	-8(3)	-19(2)
C(13)	45(3)	28(2)	44(3)	-5(2)	13(2)	-5(2)
C(14)	59(3)	41(3)	51(3)	-12(2)	8(2)	-5(2)

C(15)	56(3)	31(3)	55(3)	-8(2)	9(2)	6(2)
C(16)	63(3)	31(2)	48(3)	-5(2)	21(2)	-10(2)
C(17)	65(3)	40(3)	56(3)	-5(2)	29(3)	-11(2)
C(18)	72(3)	58(3)	48(3)	7(3)	11(3)	-14(3)

Table S10: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **2**.

	x	y	z	U(eq)
H	4250(40)	6690(20)	5570(30)	46(12)
H(1)	2290(40)	7940(20)	6110(30)	24(12)
H(2)	3778	8487	8586	48
H(3A)	3682	9083	5588	51
H(3B)	4099	8876	4604	51
H(4A)	1750	8455	4616	52
H(4B)	2672	7802	4312	52
H(5A)	1292	6829	4798	55
H(5B)	366	7459	5144	55
H(6A)	418	6213	5965	55
H(6B)	816	6921	6708	55
H(7)	6840	8278	4901	50
H(8A)	4897	7068	4137	67
H(8B)	6009	7363	3604	67
H(8C)	4801	7920	3711	67
H(9A)	8028	7353	6099	89
H(9B)	8057	7117	5017	89
H(9C)	7015	6701	5522	89
H(10)	5703	9023	7106	54
H(11A)	7641	9299	6002	91
H(11B)	7210	9884	6733	91
H(11C)	6132	9664	5720	91
H(12A)	7154	8015	7878	93
H(12B)	7876	8836	8081	93

H(12C)	8250	8267	7308	93
H(13)	2295	4859	6453	47
H(14A)	1165	5416	4925	77
H(14B)	2132	4735	4753	77
H(14C)	2612	5605	4719	77
H(15A)	4823	5202	5983	73
H(15B)	4249	4362	6091	73
H(15C)	4761	4898	7032	73
H(16)	2756	6476	8362	55
H(17A)	1370	5523	8777	77
H(17B)	1365	5040	7820	77
H(17C)	594	5847	7719	77
H(18A)	3983	4996	8419	91
H(18B)	4015	5532	9338	91
H(18C)	4861	5771	8580	91

Table S11: Torsion angles [°] for **2**.

Fe(1)-O(2)-C(2)-O(3)	7.0(7)
C(7)-P(1)-C(3)-C(4)	99.5(3)
C(10)-P(1)-C(3)-C(4)	-150.0(3)
Fe(1)-P(1)-C(3)-C(4)	-26.1(3)
C(5)-N(1)-C(4)-C(3)	-179.2(3)
Fe(1)-N(1)-C(4)-C(3)	-46.6(4)
P(1)-C(3)-C(4)-N(1)	45.3(4)
C(4)-N(1)-C(5)-C(6)	177.3(3)
Fe(1)-N(1)-C(5)-C(6)	44.5(5)
N(1)-C(5)-C(6)-P(2)	-48.2(4)
C(16)-P(2)-C(6)-C(5)	155.2(3)
C(13)-P(2)-C(6)-C(5)	-95.0(3)
Fe(1)-P(2)-C(6)-C(5)	31.4(3)
C(3)-P(1)-C(7)-C(9)	-169.9(3)
C(10)-P(1)-C(7)-C(9)	83.8(3)
Fe(1)-P(1)-C(7)-C(9)	-54.7(3)
C(3)-P(1)-C(7)-C(8)	-47.6(4)
C(10)-P(1)-C(7)-C(8)	-153.8(3)
Fe(1)-P(1)-C(7)-C(8)	67.6(3)
C(3)-P(1)-C(10)-C(12)	170.4(4)
C(7)-P(1)-C(10)-C(12)	-80.5(4)
Fe(1)-P(1)-C(10)-C(12)	58.0(4)
C(3)-P(1)-C(10)-C(11)	-60.1(4)
C(7)-P(1)-C(10)-C(11)	49.1(4)
Fe(1)-P(1)-C(10)-C(11)	-172.5(3)
C(6)-P(2)-C(13)-C(15)	165.2(3)
C(16)-P(2)-C(13)-C(15)	-87.7(3)

Fe(1)-P(2)-C(13)-C(15)	50.2(4)
C(6)-P(2)-C(13)-C(14)	41.4(4)
C(16)-P(2)-C(13)-C(14)	148.5(3)
Fe(1)-P(2)-C(13)-C(14)	-73.6(3)
C(6)-P(2)-C(16)-C(18)	174.6(3)
C(13)-P(2)-C(16)-C(18)	63.8(4)
Fe(1)-P(2)-C(16)-C(18)	-74.2(3)
C(6)-P(2)-C(16)-C(17)	47.4(4)
C(13)-P(2)-C(16)-C(17)	-63.4(4)
Fe(1)-P(2)-C(16)-C(17)	158.6(3)

Table S12: Hydrogen bonds for **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(3)	0.81(4)	2.03(4)	2.808(5)	161(4)

6. References

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