Homoleptic mono-, di-, and tetra-iron complexes featuring phosphido ligands: a synthetic, structural, and spectroscopic study.

*Kinga Kaniewska[a], Łukasz Ponikiewski[a], Natalia Szynkiewicz[a], Bartłomiej Cieślik[b], Jerzy Pikies[a], J. Krzystek[c], Alina Dragulescu-Andrasi[d], Sebastian A. Stoian[e] and Rafał Grubba[a]**

[a] Department of Inorganic Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 11/12 Gabriela Narutowicza St. 80-233 Gdańsk, Poland

[b] Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 11/12 Gabriela Narutowicza St. 80-233 Gdańsk, Poland

[c] National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USA

[d] Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA

[e] Department of Chemistry, University of Idaho, Moscow, ID 83844, USA

Supporting Information

Table of Contents

1. Crystallographic details

Table S1. Crystallographic data of **1**, **2** and **3**

	1	**2**	**3**
Name in cif file	15168ocg	kk18ipds	kk48
CCDC no.	1911161	1911163	1911164
Empirical formula	$C_{44}H_{102}Fe_2LiO_6P_4$ [1 ($C_{32}H_{72}Fe_2P_4$), 1($C_{12}H_{30}LiO_6$]	$C_{126}H_{205}Fe_4Li_2O_{13}P_{10}$ [2 ($C_{50}H_{70}Fe_2P_5$), 2 ($C_{12}H_{30}LiO_6$), 0.5 ($C_4H_{10}O_2$)]	$C_{74}H_{145}Fe_2LiO_7P_5$ [1 ($C_{60}H_{110}Fe_2P_5$), 1 ($C_{12}H_{30}O_6Li$), 0.5 ($C_4H_{10}O_2$)]
M_r/g mol^{-1}	969.77	2474.87	1420.38
Temperature (K)	150(2)	120(2)	120(2)
Wavelength (Å) (Mo/Cu *K*α)	1.54184 (Cu*K*α)	0.71073 (Mo*K*α)	0.71073 (Mo*K*α)
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	*P* $2_1/n$	$P\bar{1}$	*P n n* 2
a (Å)	16.3033(2)	11.8564(3)	23.6571(2)
b (Å)	18.5678(2)	22.9887(6)	25.8470(4)
c (Å)	19.4935(2)	25.0177(7)	13.2128(6)
α (°)	90	86.698(2)	90
β (°)	104.1070(10)	89.512(2)	90
γ (°)	90	83.754(2)	90
V (Å^3)	5723.04(11)	6767.2(3)	8079.2(4)
Z	4	2	4
F(000)	2116	2650	3100
R_{int}	0.0316	0.0441	0.0451
D_{Calc} (Mg m^{-3})	1.126	1.215	1.168
Crystal size (mm)	0.4798 x 0.4760 x 0.2721	0.22 x 0.21 x 0.19	0.22 x 0.22 x 0.20
μ (mm^{-1})	5.408	0.593	0.505
θ Range (°)	3.65 – 62.612	2.38 – 27.19	2.70 – 29.46
Reflections collected/unique	31171/9133	52159/28177	83344/21750
Completeness to θ_{max} (%)	99.7	96.5	98.6
Data/restraints/parameters	9133/0/557	28177/9/1420	21750 /45/727
Goodness-of-fit on F^2	1.02	1.028	1.053
Final R indices [I>2σ(I)] R indices (all data)	R_1 = 0.0347 wR_2 = 0.0882 R_1 = 0.0384 wR_2 = 0.0907	R_1 = 0.0521 wR_2 = 0.1273 R_1 = 0.0866 wR_2 = 0.1509	R_1 = 0.058 wR_2 = 0.1421 R_1 = 0.0814 wR_2 = 0.1547
Largest difference peak and hole (e Å^{-3})	0.48 and -0.388	1.213 and -0.673	0.831 and -0.588

Table S2. Crystallographic data of **4** and **5**

	4	**5**
Name in cif file	kk2ipds	raf5
CCDC no.	1911162	1911165
Empirical formula	$C_{41}H_{96}Fe_4P_6$ [1 ($C_{36}H_{84}Fe_4P_6$), 1 (C_5H_{12})]	$C_{45}H_{111}FeO_6P_6Si_3Li$ [1 ($C_{33}H_{81}FeP_6Si_3$), 1 ($C_{12}H_{30}O_6Li$)]
M_r/g mol^{-1}	998.39	1074.27
Temperature (K)	120(2)	121(2)
Wavelength (Å) (Mo/Cu *K*α)	0.71073 (Mo*K*α)	0.71073 (Mo*K*α)
Crystal system	Trigonal	Monoclinic
Space group	$R\bar{3}$	*P* $2_1/c$
a (Å)	18.1444(11)	17.6278(6)
b (Å)	18.1444(11)	17.5183(7)
c (Å)	26.8759(16)	24.0113(8)
α (°)	90	90
β (°)	90	94.002(3)
γ (°)	120	90
V (Å^3)	7662.6(10)	7396.8(5)
Z	6	4
F(000)	3216	2348
R_{int}	0.0369	0.0849
D_{Calc} (Mg m^{-3})	1.298	0.965
Crystal size (mm)	0.2 x 0.2 x 0.18	0.22 x 0.21 x 0.21
μ (mm^{-1})	1.327	0.414
θ Range (°)	3.20 – 29.56	3.5210 – 26.6180
Reflections collected/unique	6403/3683	116535 /16119
Completeness to θ_{max} (%)	98.5	99.7
Data/restraints/parameters	3683/0/230	16119/0/414
Goodness-of-fit on F^2	0.996	1.05
Final R indices [I>2σ(I)] R indices (all data)	R_1 = 0.0355 wR_2 = 0.0941 R_1 = 0.052 wR_2 = 0.0998	R_1 = 0.0911 wR_2 = 0.2325 R_1 = 0.1346 wR_2 = 0.2647
Largest difference peak and hole (e Å^{-3})	0.395 and -0.414	2.609 and -0.613

2. NMR spectra

^{1}H NMR spectra of isolated compounds

COMPLEX 1

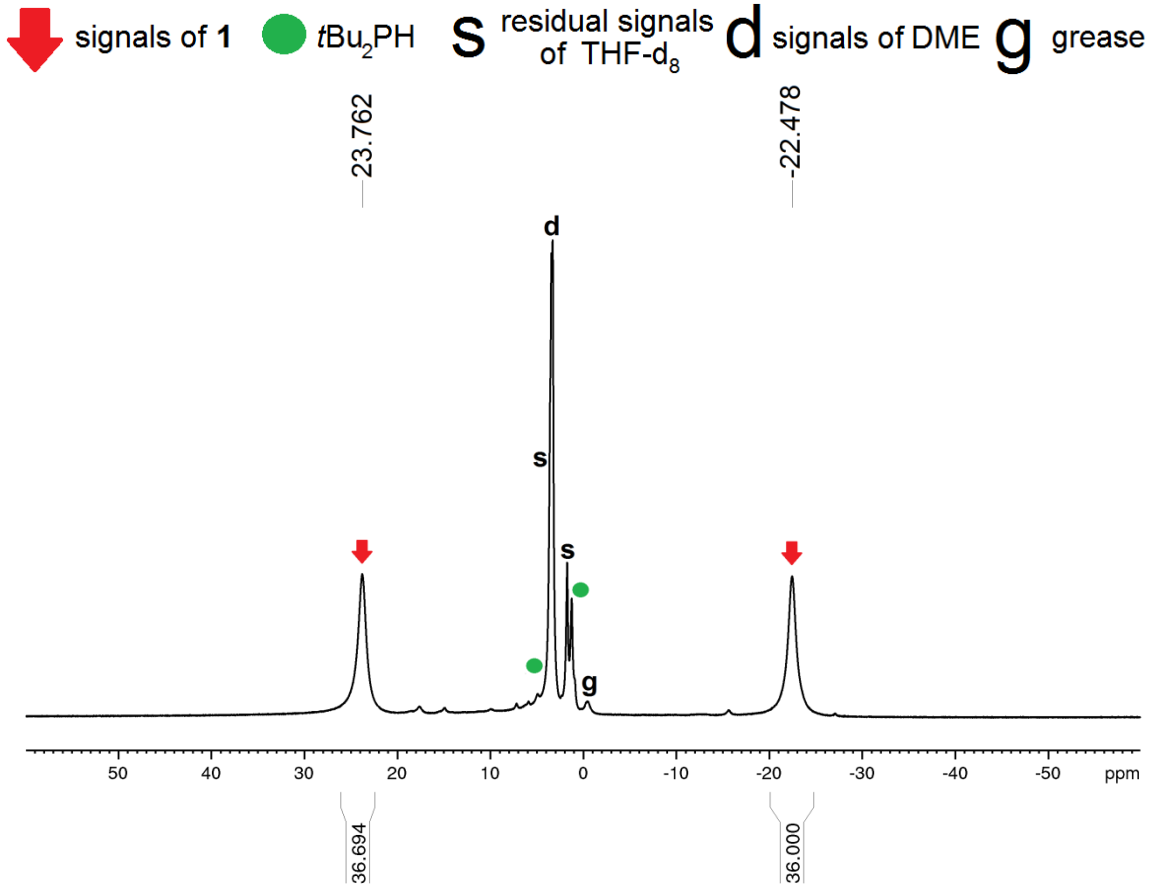

Figure S1. ^{1}H NMR spectrum of **1** at room temperature.

COMPLEX 2

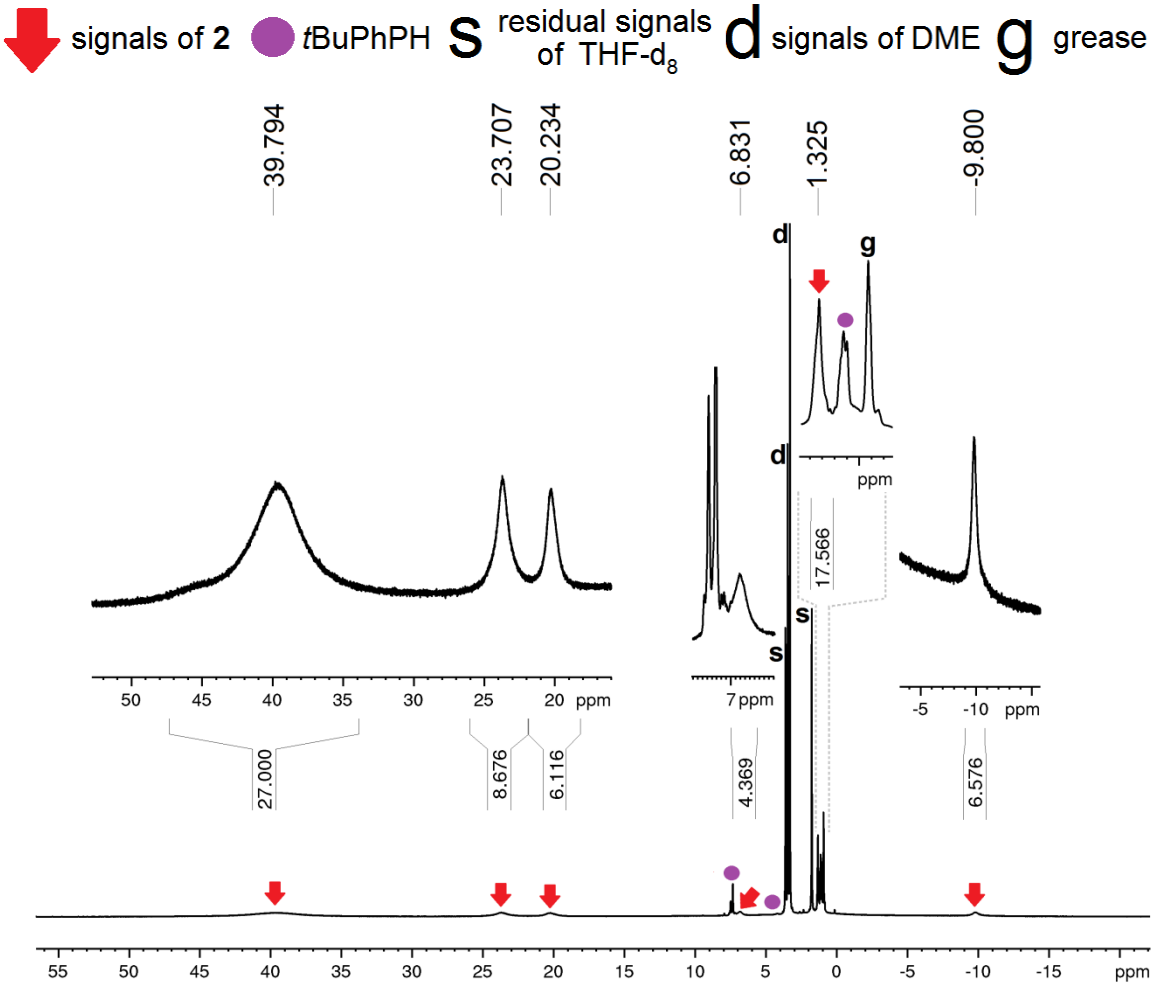

Figure S2. ^{1}H NMR spectrum of **2** at room temperature.

COMPLEX 3

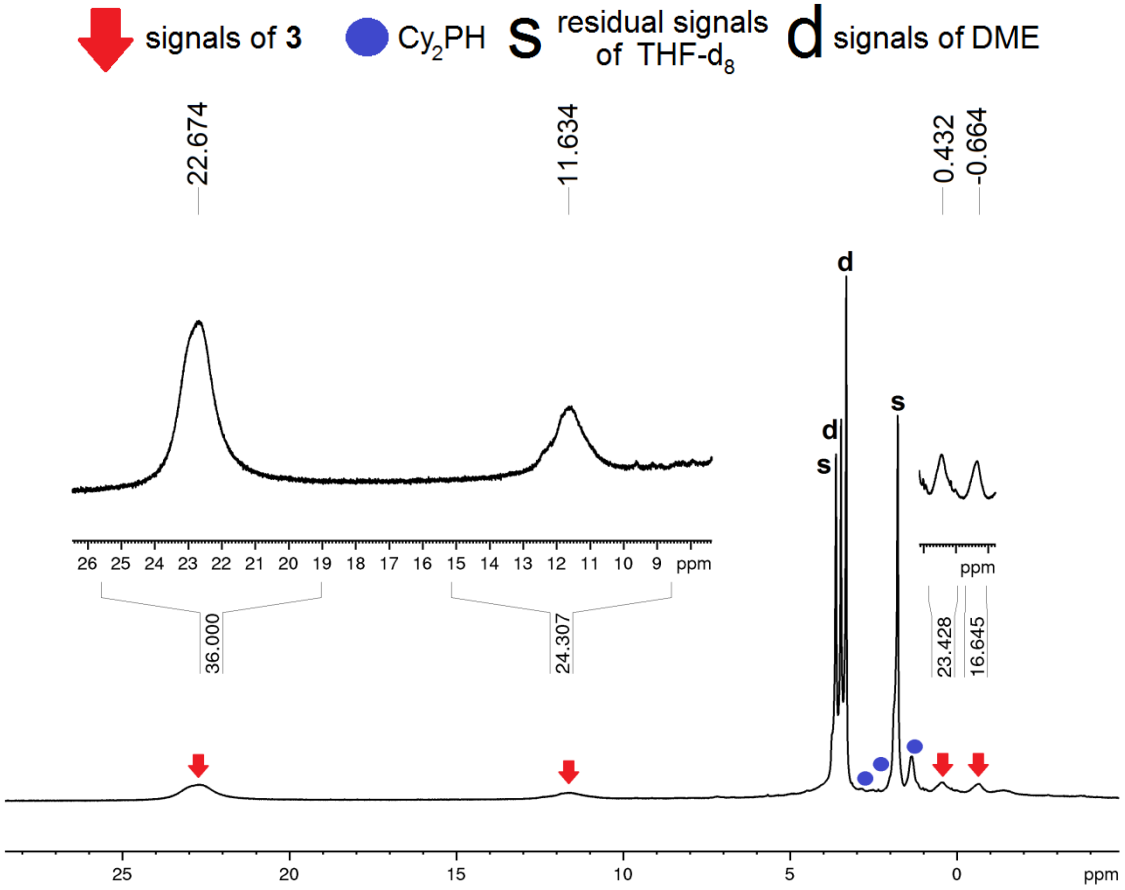

Figure S3. ^{1}H NMR spectrum of **3** at room temperature.

$^{31}P\{^{1}H\}$ NMR spectra of reaction mixtures

COMPLEX 1

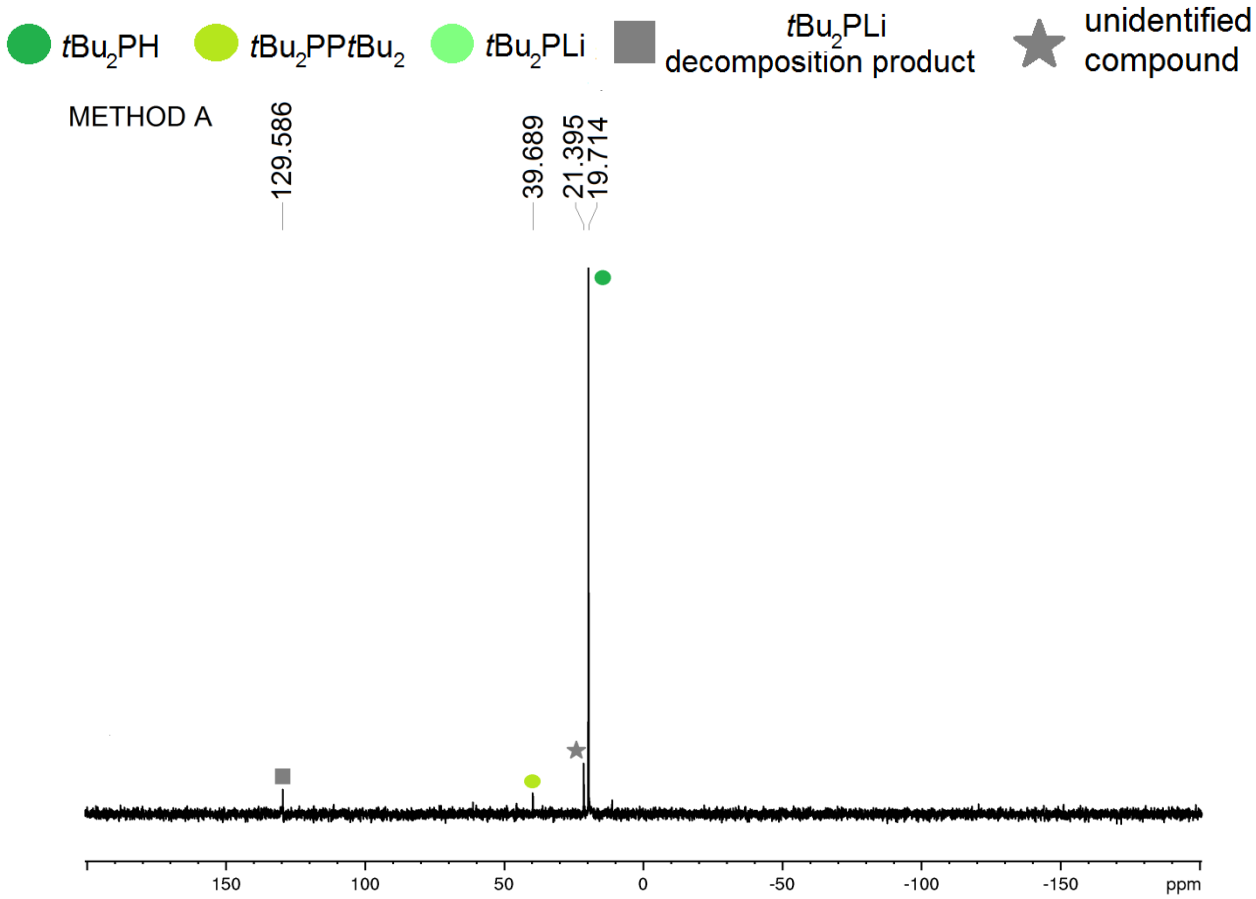

Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture resulting from mixing [(Dippnacnac)$FeCl_2Li(dme)_2$] with *t*Bu_2PLi in the molar ratio 1:3 – method A of complex **1** synthesis.

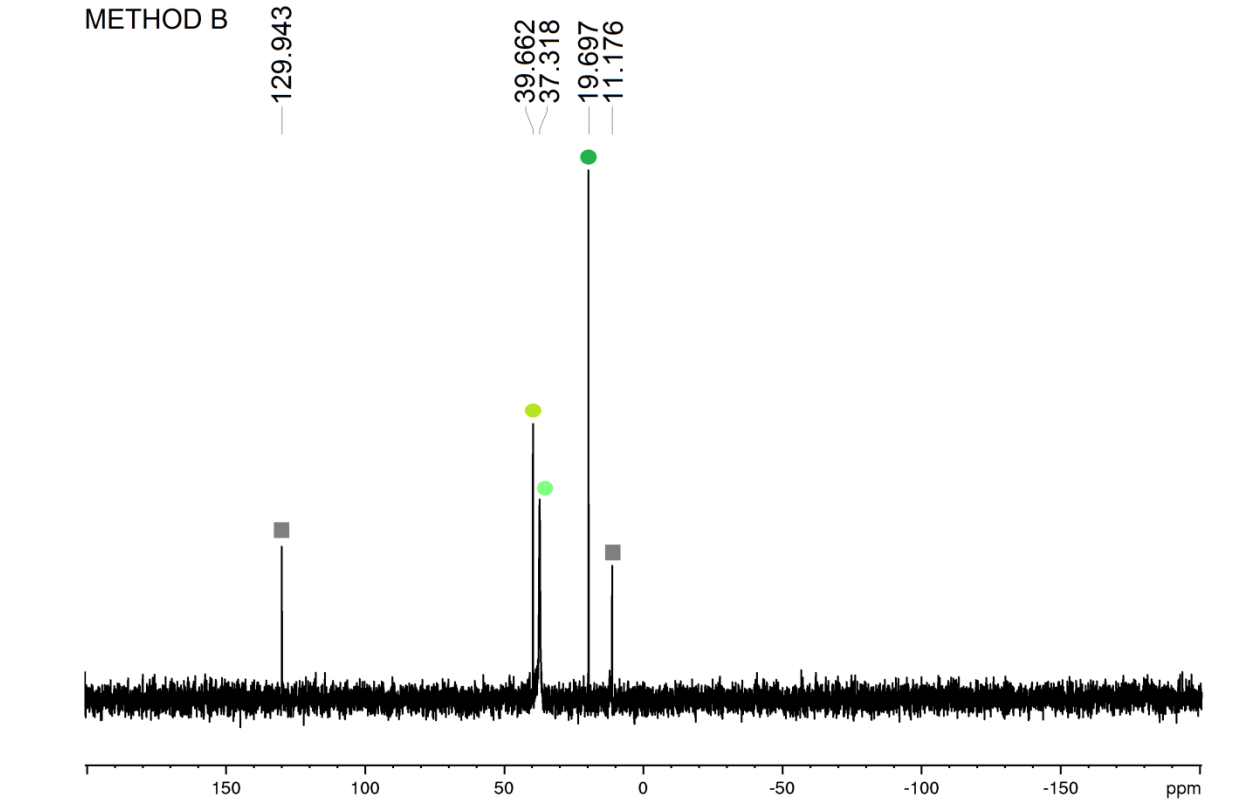

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture resulting from mixing [$FeBr_2(thf)_2$] with *t*Bu_2PLi in the molar ratio 1:4 – method B of complex **1** synthesis.

COMPLEX 2

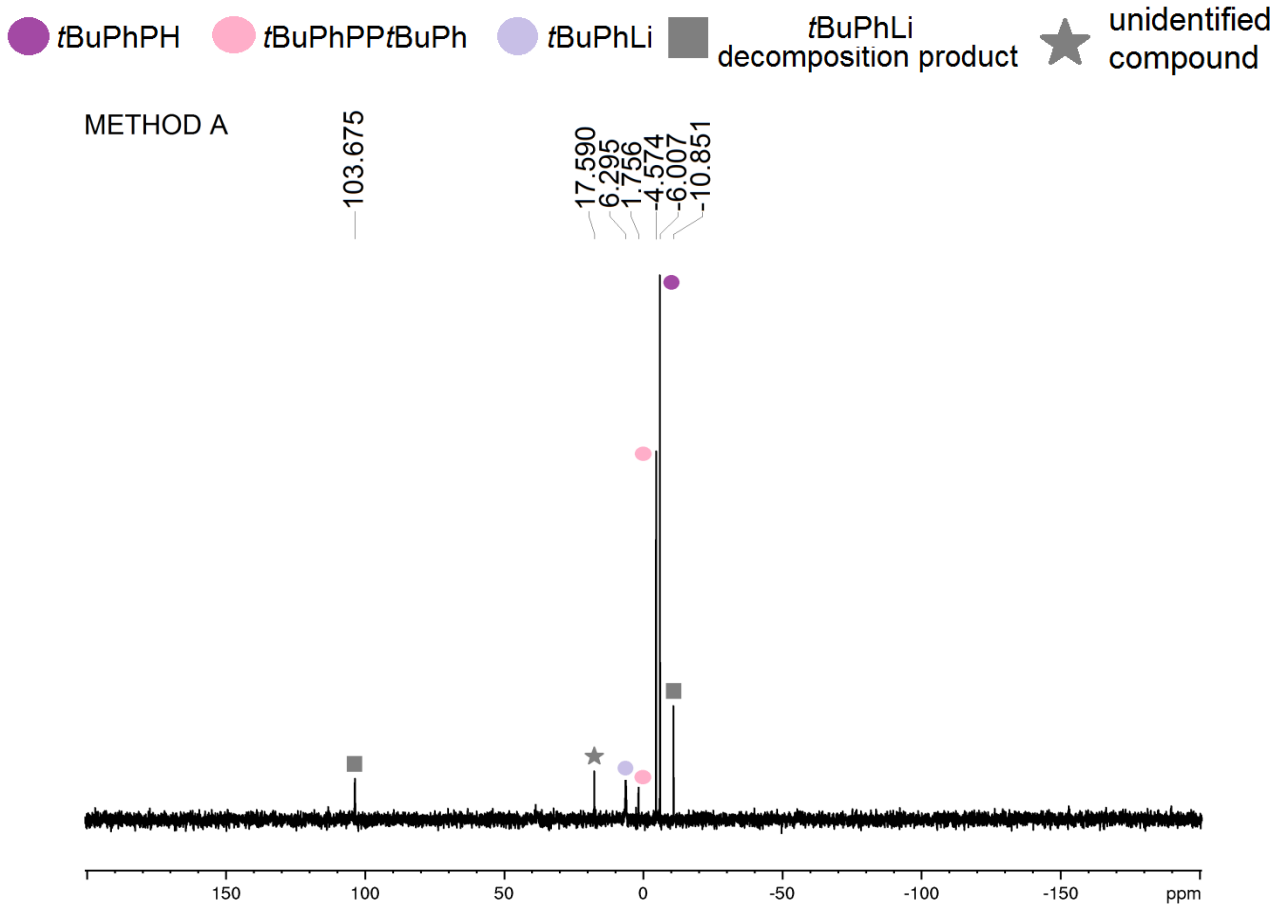

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture resulting from mixing $[(Dippnacnac)FeCl_2Li(dme)_2]$ with *t*BuPhPLi in the molar ratio 1:3 – method A of complex **2** synthesis.

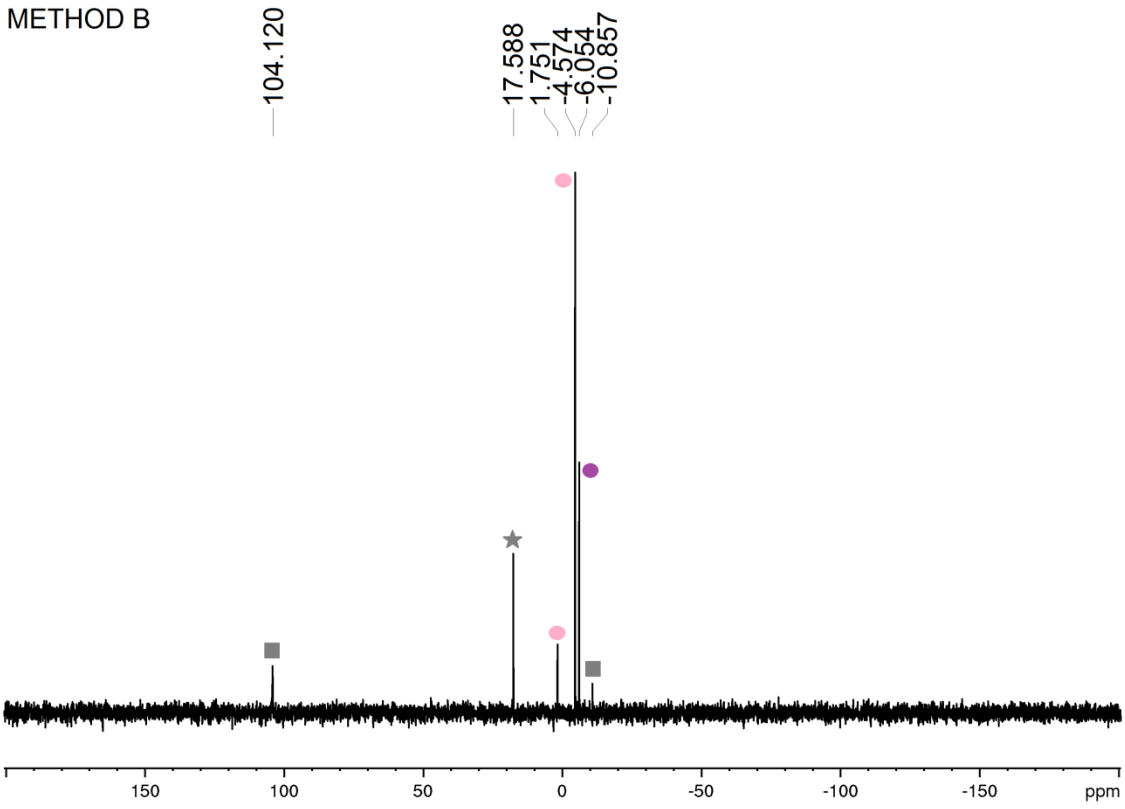

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture resulting from mixing $[FeBr_2(thf)_2]$ with *t*BuPhPLi in the molar ratio 1:3 – method B of complex **2** synthesis.

COMPLEX 3

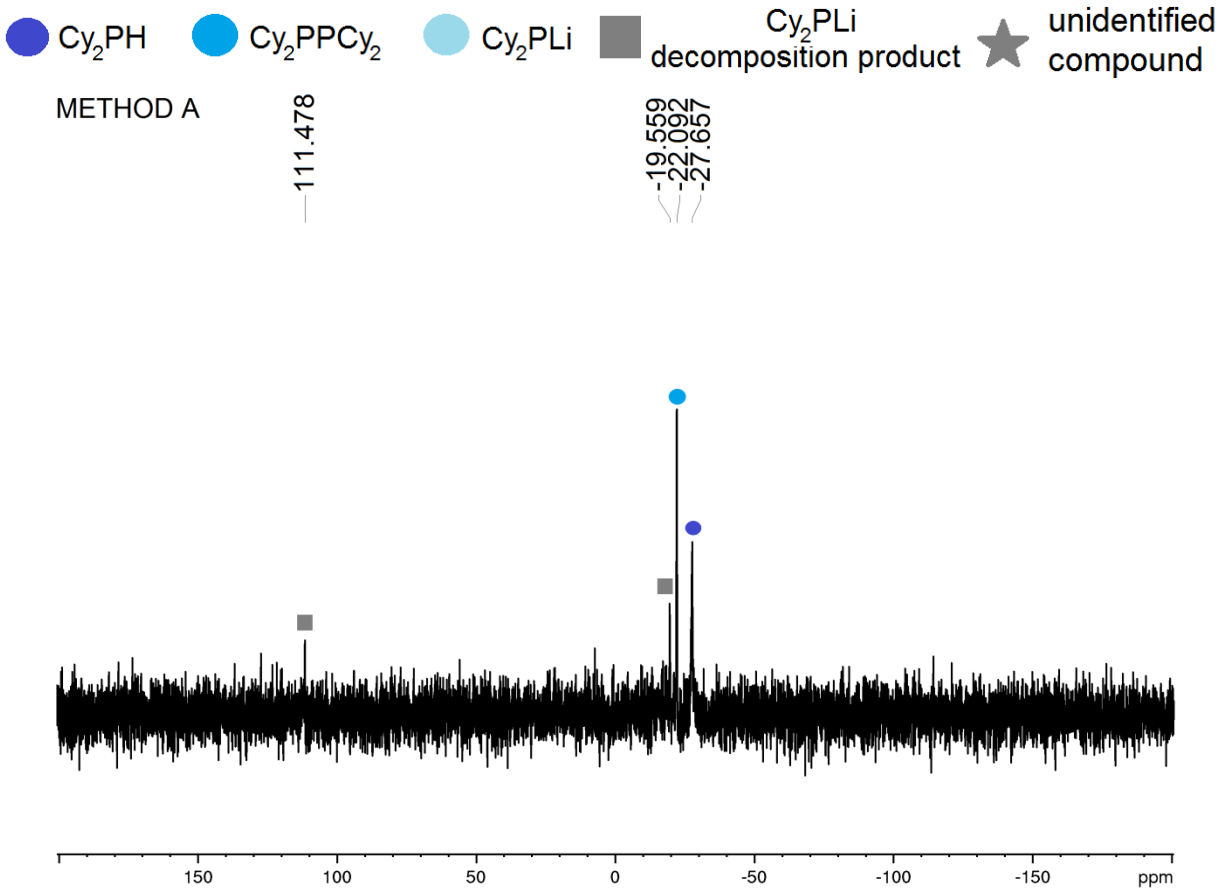

Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture resulting from mixing [(Dippnacnac)$FeCl_2Li(dme)_2$] with Cy_2PLi in the molar ratio 1:3 – method A of complex **3** synthesis.

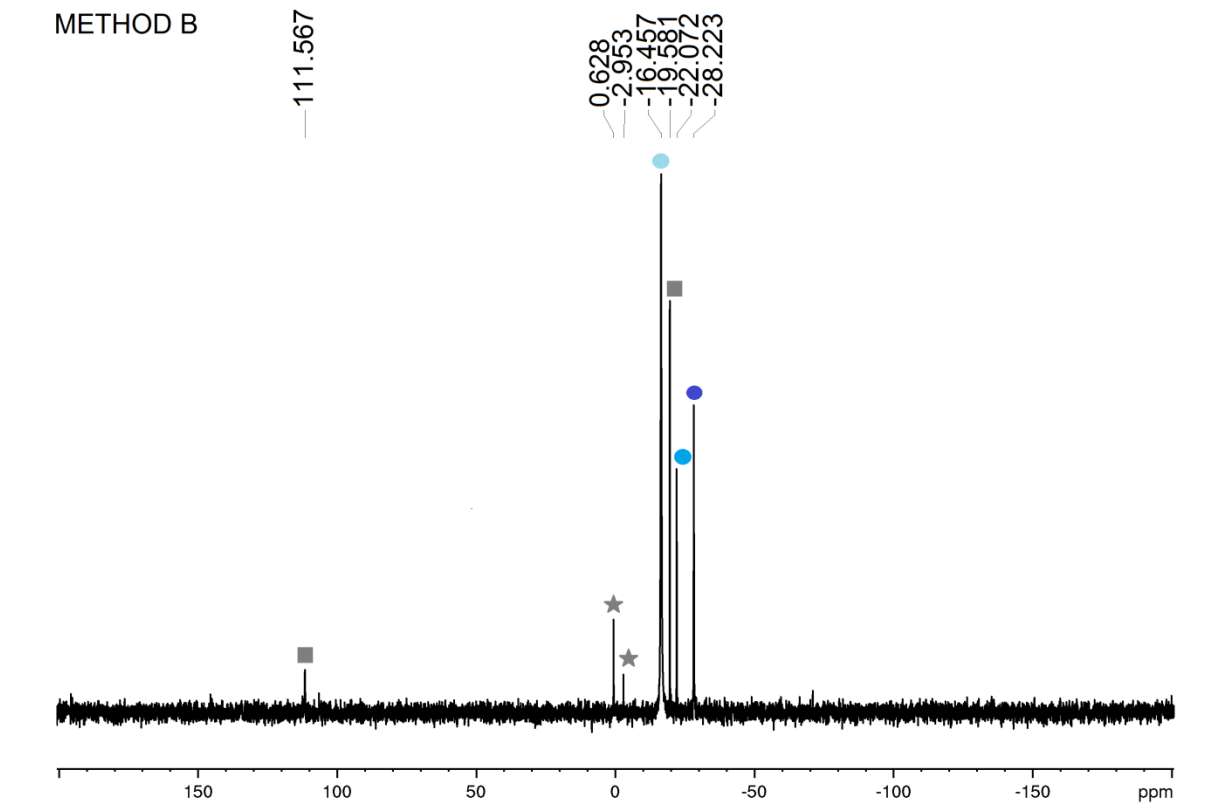

Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture resulting from mixing [$FeBr_2(thf)_2$] with Cy_2PLi in the molar ratio 1:6 – method B of complex **3** synthesis.

COMPLEX 4

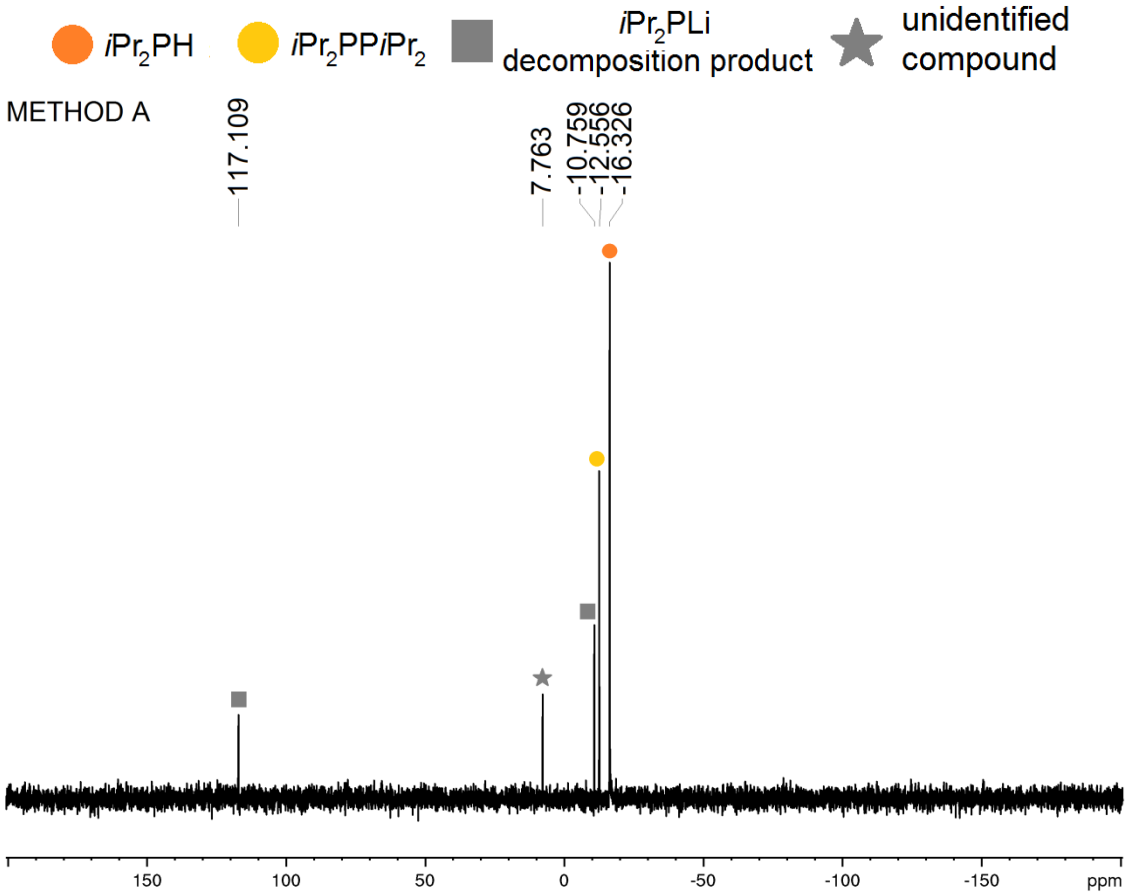

Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture resulting from mixing [(Dippnacnac)$FeCl_2Li(dme)_2$] with *i*Pr_2PLi in the molar ratio 1:3 – method A of complex **4** synthesis.

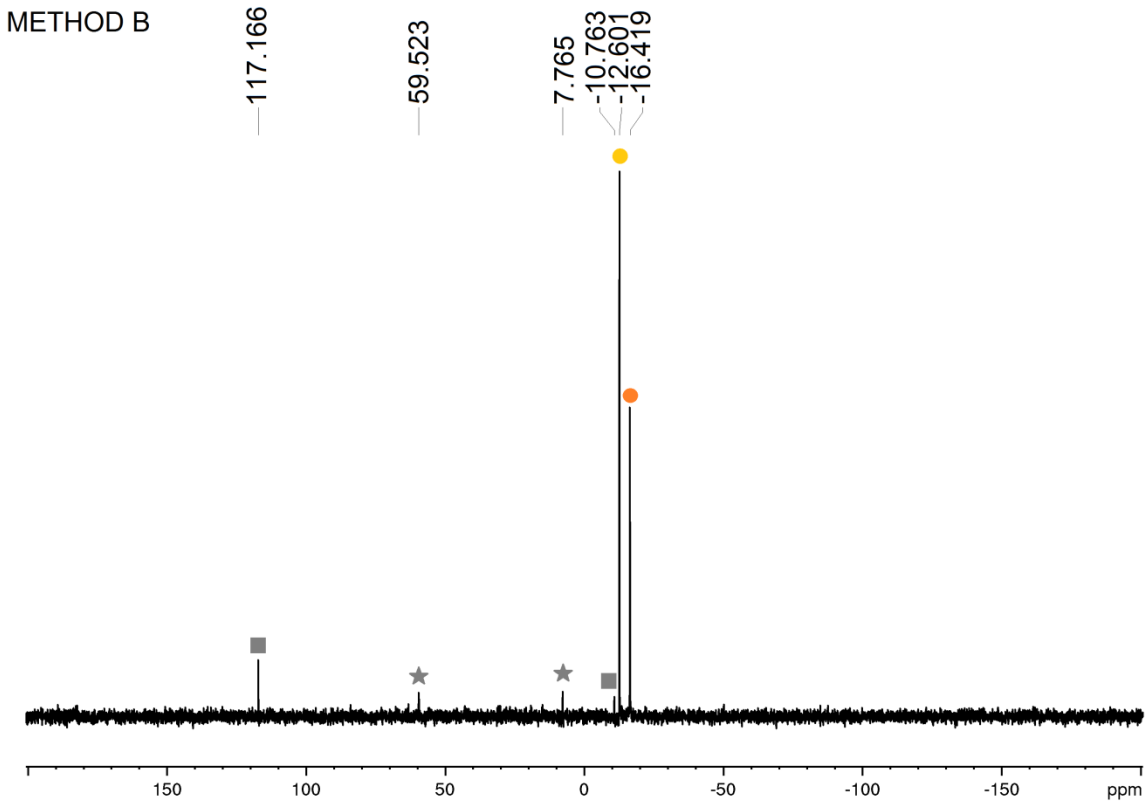

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture resulting from mixing [$FeBr_2(thf)_2$] with *i*Pr_2PLi in the molar ratio 1:6 – method B of complex **4** synthesis.

COMPLEX 5

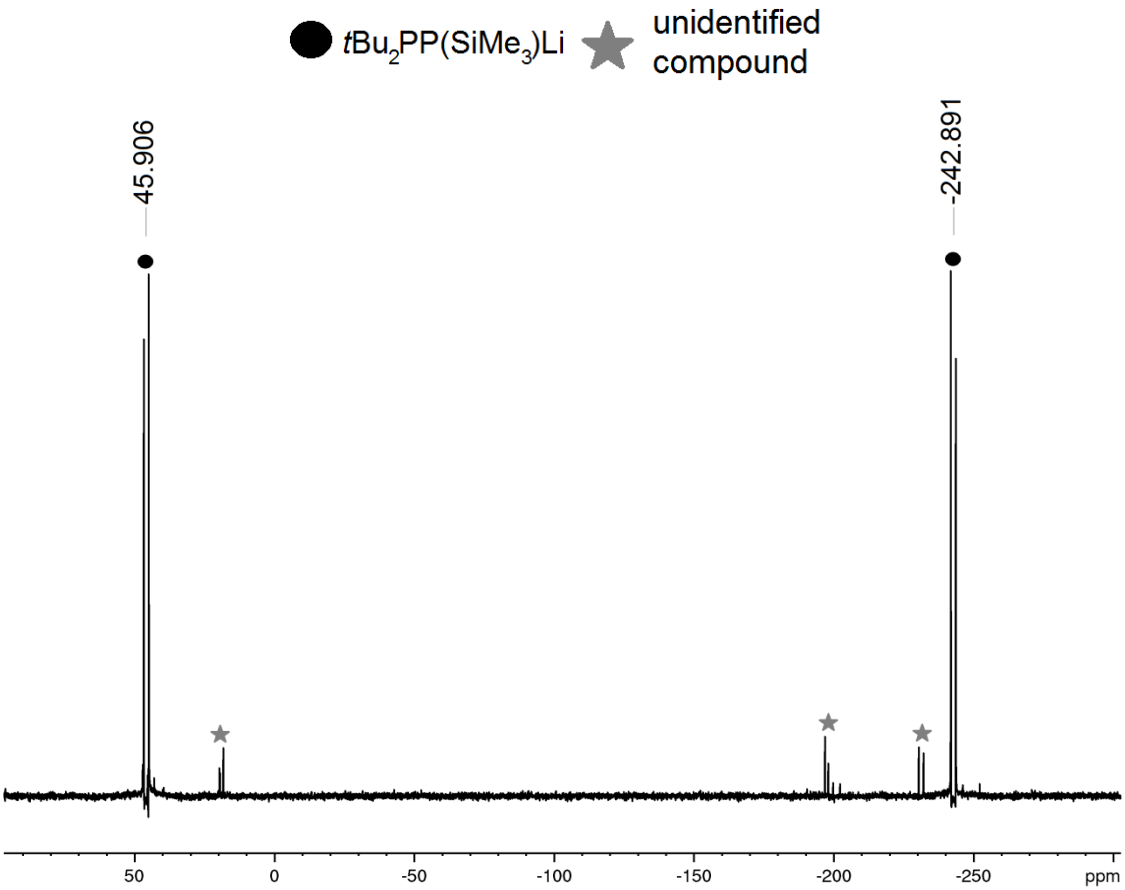

Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture resulting from mixing [(Dippnacnac)$FeCl_2Li(dme)_2$] with *t*$Bu_2PP(SiMe_3)Li$ in the molar ratio 1:2.43 – synthesis of complex **5**.

3. Yields of 1-4 iron complex syntheses

Table S3. Yields of **1**-**4** iron complex syntheses.

Method	Ratio $Fe^{II}_{starting\ complex}$: R_2PLi	Phosphide			
		t-Bu_2PLi	*t*-BuPhPLi	Cy_2PLi	*i*-Pr_2PLi
A	1:1	**1** (a few crystals isolated)	product not isolated	[(Dippnacnac)Fe(Cl)PCy_2Li$(dme)_2$] (53%)[1]	[(Dippnacnac)Fe(Cl)*i*-Pr_2][Li$(dme)_3$] (46%)[1]
	1:2	**1** (8%)	product not isolated	[(Dippnacnac)Fe(Cl)PCy_2][Li$(dme)_3$](44%)[1]	colorless crystals
	1:3	**1** (18%)	**2** (39%)	**3** (86%)	**4** (58%)
	1:6	product not isolated	**2** (20%)	x	product not isolated
B	1:3	product not isolated	**2** (64%)	colorless crystals	**4** (3%)
	1:4	**1** (65%)	x	**3** (6%)	x
	1:6	x	**2** (35%)	**3** (8%)	product not isolated

x – reaction was not done

– the best yield of the homoleptic iron complexes synthesis

4. Magnetic measurements in the solution – Evans Method

Effective magnetic moments μ_{eff} of **1**-**3** paramagnetic complexes in the solution were determined by ^{1}H NMR spectroscopy using the Evans Method[2] with pure solvent (THF-d_8) as internal reference and not neglecting diamagnetic contributions according to below presented equations.[3]

$$\chi_{\mathrm{meas}} = \chi_{\mathrm{p}} + \chi_{\mathrm{d}}$$

$$\chi_{\mathrm{meas}} = \frac{3 \cdot \Delta f}{4 \cdot \pi \cdot F \cdot c}$$

$$\chi_{\mathrm{d}} = -\frac{\mathrm{M}}{2} \cdot 10^{-6}$$

$$\chi_{\mathrm{p}} = \chi_{\mathrm{meas}} - \chi_{\mathrm{d}}$$

$$\mu_{eff} = \sqrt{8 \cdot T \cdot \chi_{\mathrm{p}}}$$

where

χ_{meas} – total measured magnetic susceptibility $\left[\frac{\mathrm{emu}}{\mathrm{mol}}\right]$

χ_{p} – paramagnetic susceptibility $\left[\frac{\mathrm{emu}}{\mathrm{mol}}\right]$

χ_{d} – diamagnetic susceptibility $\left[\frac{\mathrm{emu}}{\mathrm{mol}}\right]$

Δf – chemical shift difference between solvent in presence of paramagnetic compound and in pure solvent [Hz]

F – operating frequency of NMR spectrometer [Hz]

c – concentration of paramagnetic solution $\left[\frac{\mathrm{mol}}{\mathrm{mL}}\right]$

M – molar mass of paramagnetic compound $\left[\frac{\mathrm{emu}}{\mathrm{mol}}\right]$

T – temperature during measurement [K]

μ_{eff} – effective magnetic moment [μ_B]

$\pi \approx 3.14$

Note: emu is the most widely used unit for the magnetic susceptibility, $1\ \mathrm{emu} = 1\ \mathrm{cm}^3 = 1\ \mathrm{mL}$

5. MP-AES measurements

Table S4. Content of LiX impurity in crystalline samples of **1**-**3**.

Sample of complex	Mass of sample [g]	Found total Li content [mg/g]	Found molar ratio: complex : LiX (MP-AES)	Found molar ratio: complex : LiX (microanalysis)
1	0.0527	11.49 ± 0.74	0.87	1
2	0.0554	8.5 ± 1.2	0.51	0.5
3	0.0547	8.99 ± 0.33	0.92	1

6. DFT calculations

All calculations presented in the paper were performed using the Gaussian 09[4] program package using density functional theory at the ωB97XD functional by Head-Gordon[5,6] with 6-31+G(d,p) basis set for P and LANL2DZ for Fe, C and H atoms. Geometries of complexes **1**-**3** were obtained from X-ray and these experimental, non-optimized coordinates were used for all single points calculations including Natural Bonding Orbitals (NBO), Hirshfeld population analysis[7], Mayer Bond Order analysis.[8] Natural Bonding Orbitals (NBO, version 6.0)[9] analysis was performed for all systems including calculations of Natural Localized Molecular Orbitals (NLMO)[10] and Natural Population Analysis (NPA)[11]. In order to determine the number of unpaired electrons in complexes 1-3, single point calculations were performed for three selected multiplicities of the system. The number of unpaired electrons in the molecule and consequently the spin multiplicity (**M**) of the system was calculated as **M = 2S + 1** where **S** is total spin quantum number equal to **n/2** and n is number of unpaired electrons. The lowest-energy of the system is obtained for the correct spin-state of the given geometry (Table S5).

Table S5. Electronic energy E of **1-3** iron complexes for three selected multiplicities of the system.

Complex 1		**Complex 2**		**Complex 3**	
Spin multiplicity	**E [a. u.]**	**Spin multiplicity**	**E [a. u.]**	**Spin multiplicity**	**E [a. u.]**
6	-2873.768831	5	-3899.380809	5	-4304.439083
8	-2873.764673	7	-3899.409295	7	-4304.465760
		9	-3899.393014	9	-4304.447505

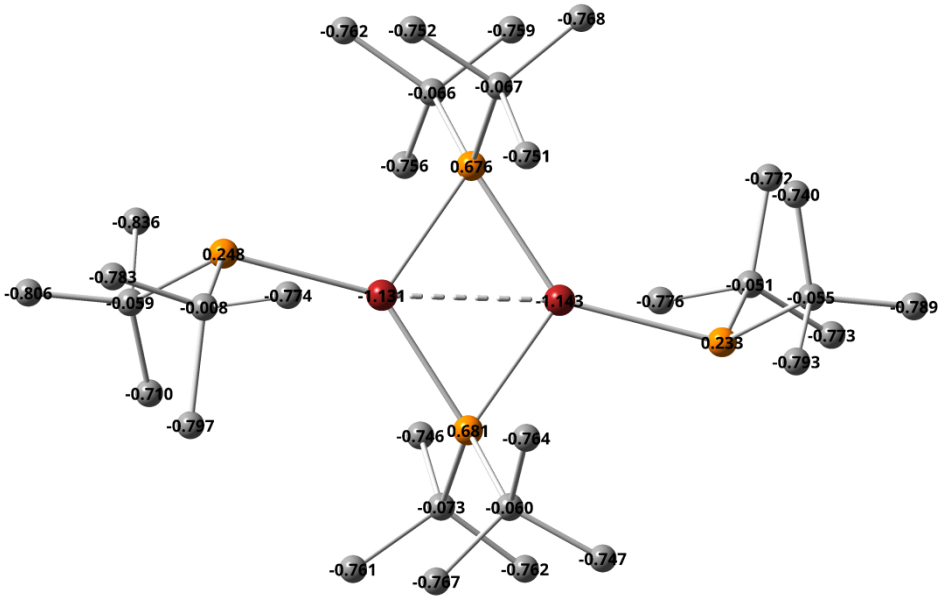

Figure S13. NPA charges of complex **1**.

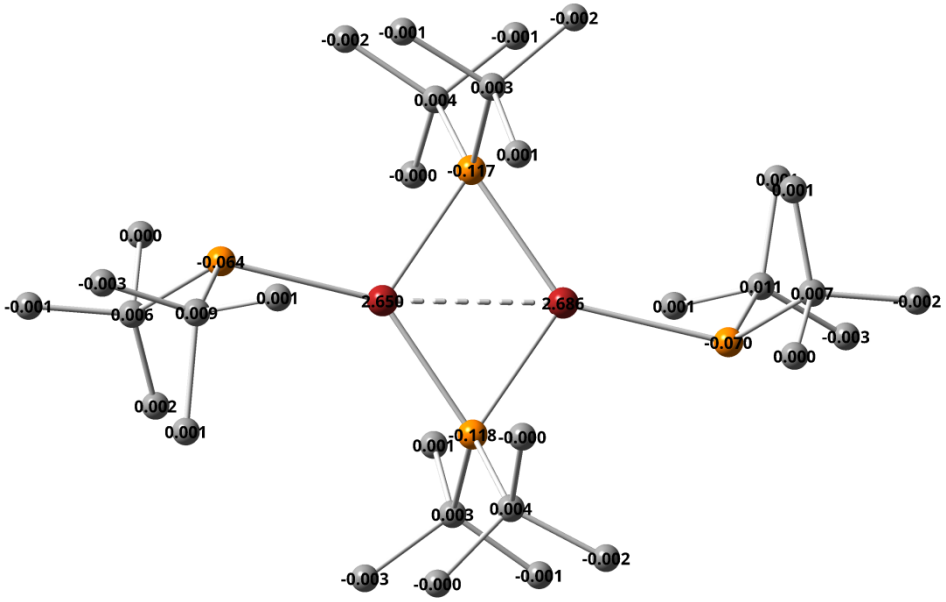

Figure S14. NPA spin densities of molecule **1**.

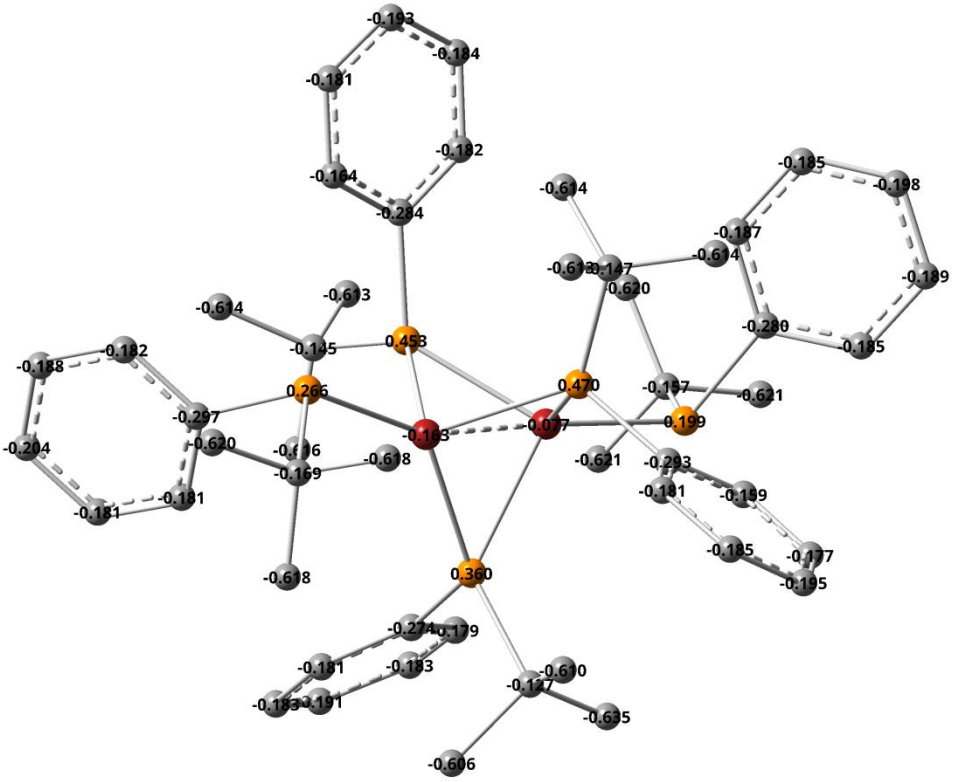

Figure S15. NPA charges of complex **2**.

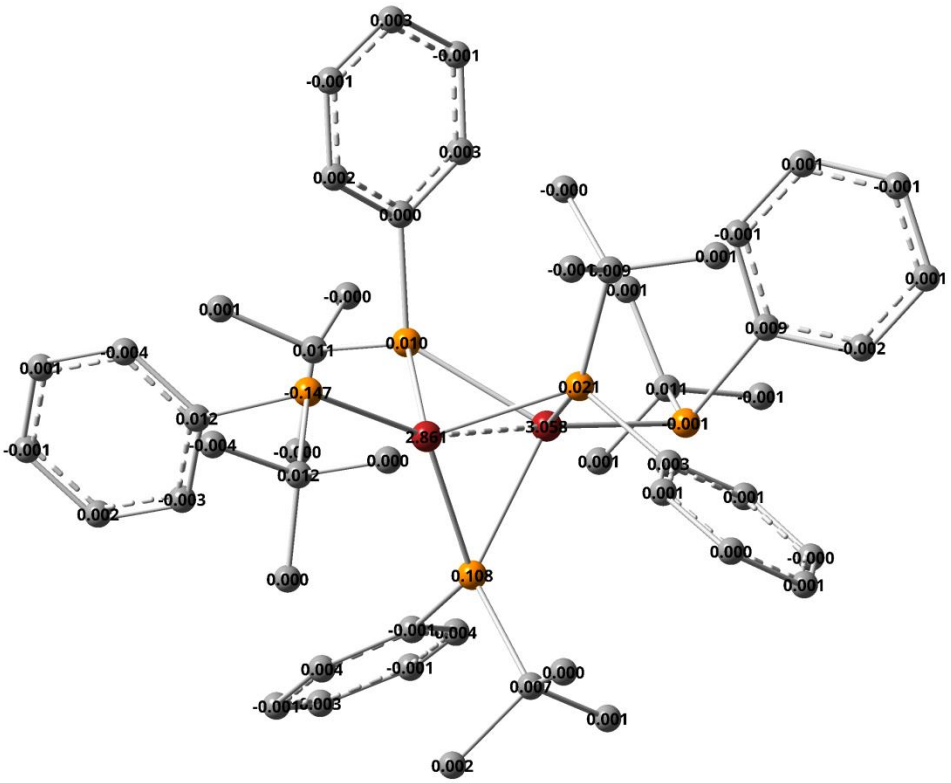

Figure S16. NPA spin densities of complex **2**.

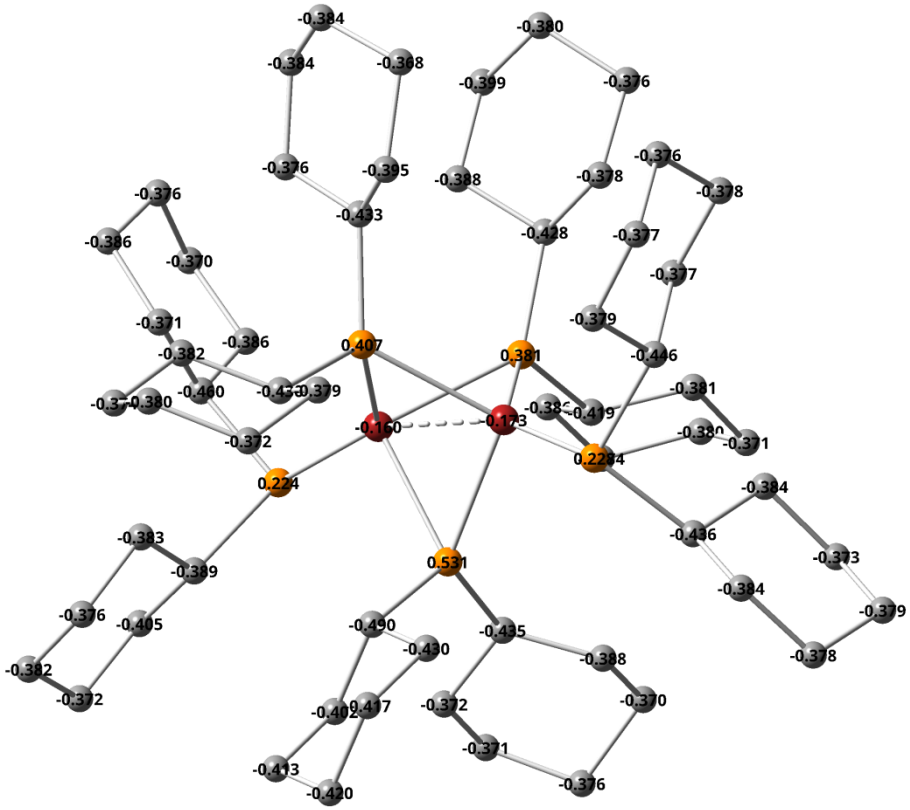

Figure S17. NPA charges of complex **3**.

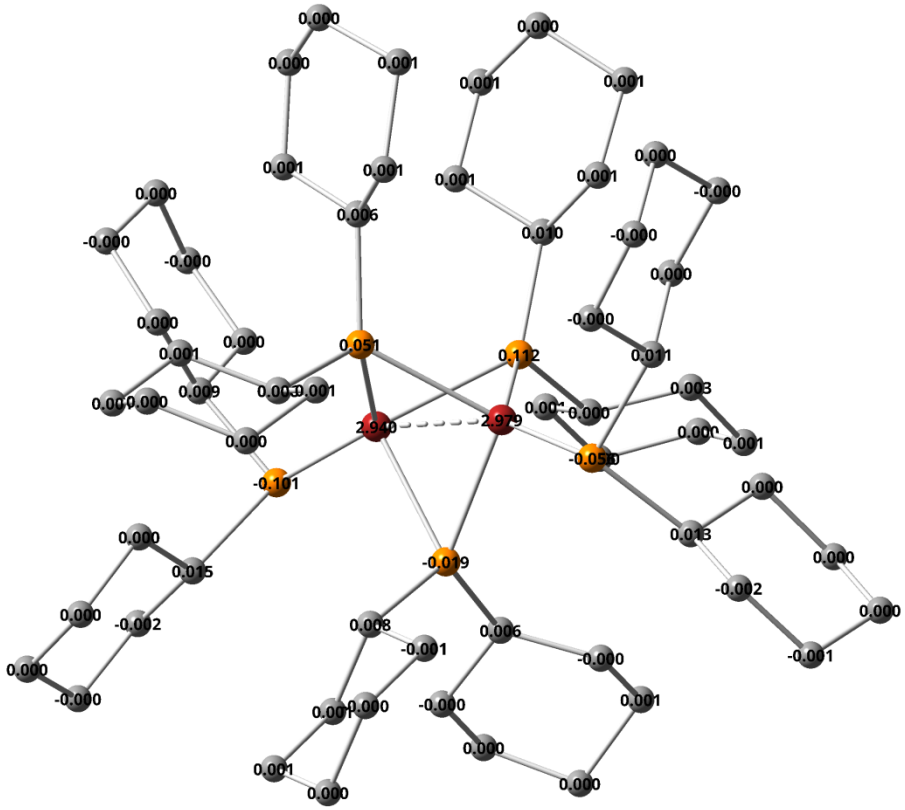

Figure S18. NPA spin densities of complex **3**.

7. References

1 K. Kaniewska, A. Dragulescu-Andrasi, Ł. Ponikiewski, J. Pikies, S. A. Stoian and R. Grubba, *Eur. J. Inorg. Chem.*, 2018, 4298–4308.

2 D. F. Evans, *J. Chem. Soc.*, 1959, 2003–2005.

3 G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532–536.

4 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortritz, A. F. Izmaylov, J. L. Sonnenberg, F. L. D. Williams-Young, F. Ding, J. B. F. F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throsse and D. J. Fox, 2016.

5 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615.

6 S. Grimme, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2011, **1**, 211–228.

7 F. L. Hirshfeld, *Theor. Chim. Acta*, 1977, **44**, 129–138.

8 I. Mayer, *Chem. Phys. Lett.*, 1983, **97**, 270–274.

9 E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, *NBO 6.0, Theoretical Chemistry Institute, University of Wisconsin,2013.*, .

10 A. E. Reed and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 1736–1740.

11 F. Reed, Alan E.; Weinstock, Robert B.; Weinhold, *J. Chem. Phys.*, 1985, **83**, 735–746.