Supplementary Information for:

Synthesis, structure and electrochemical properties of 3,4,5-triaryl-1,2-diphosphaferrocenes

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Experimental part

General All reactions and manipulations were carried out under dry pure N_2 in standard Schlenk apparatus. All solvents were distilled from sodium/benzophenone or phosphorus pentoxide and stored under nitrogen before use. The NMR spectra were recorded on a Bruker MSL-400 (^{1}H 400 MHz, ^{31}P 161.7 MHz, ^{13}C 100.6 MHz). $SiMe_4$ was used as internal reference for ^{1}H and ^{13}C NMR chemical shifts, and 85% H_3PO_4 as external reference for ^{31}P NMR. All experiments were carried out using standard Bruker pulse programs. Infrared (IR) spectra were recorded on a Bruker Vector-22 spectrometer. The elemental analyses were carried out at the microanalysis laboratory of the Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences.

UV-Vis Experiments Electronic absorption (UV-Vis) spectra were recorded at room temperature on a Perkin-Elmer Lambda 35 spectrometer using 10 mm quartz cells. Absorption spectra were registered with a scan speed of 480 nm/min, using a spectral width of 1 nm. All samples were prepared as solutions in dichloromethane with the concentrations ~ $2 – 5\cdot10^{-5}$ mol L^{-1}.

DFT calculations All calculations were performed with the Gaussian 16 suite of programs.[1] The hybrid PBE0 functional[2] and the Ahlrichs' triple-ζ def-TZVP AO basis set[3] were used for optimization of all structures. In all geometry optimizations, the D3 approach[4] was applied to describe the London dispersion interactions as implemented in the Gaussian 16 program. Time-dependent density functional response theory (TD-DFT) with the use of long-range-corrected CAM-B3LYP functional[5] has been employed to compute the vertical excitation energy (i.e., absorption wavelength) and oscillator strength for the ground state optimized geometries. For simulation of the solvent effects, conductor-like polarizable continuum model (C-PCM) was used as implemented in the Gaussian program.[6]

Electrochemical measurements were conducted with a BASi Epsilon EClipse electrochemical analyzer (USA). The program concerned Epsilon-EC-USB-V200 waves. A conventional three-electrode system was used with glassy carbon (GC) or carbon paste electrode (CPE) solutions for powder samples as the working electrode, the Ag/AgCl (0.01 M) electrode as the reference electrode, and a Pt wire as the counter electrode. 0.1 M Et_4NBF_4 was used as the supporting electrolyte to determine the current–voltage characteristics.

To study the powder samples, a modified CPE working electrode was used, which was prepared as follows: the carbon particles/phosphonium salt (dodecyl(tri-*tert*-butyl)phosphonium tetrafluoroborate) composite electrode was prepared by grinding a mixture of graphite powder and phosphonium salt with a 70/30 (w/w) ratio in a mortar giving a homogeneous mass.[7] A modified electrode was also devised in a similar manner except that a portion (ca. 5%) of the graphite powder was replaced by the investigated compound under study. As a result, a portion of the resulting paste was packed firmly into the Teflon holder cavity (3 mm in diameter).

X-ray single-crystal diffraction. The X-ray diffraction data for single crystals of **2a** and **2c** were collected on a Bruker AXS Kappa APEX Duo diffractometer, and for **2b** on a Rigaku Oxford Diffraction Gemini diffractometer. Data collection was performed employing an ω/φ-scan mode. The programs used were APEX3 (CrysAlis Pro)[8] for data collection, SAINT[9] for data reduction, SADABS (**2b**: SCALE3 ABSPACK implemented in CrysAlis Pro)[10] for multi-scan absorption correction, SHELXT[11] for structure solution, and SHELXL[12] for structure refinement by full-matrix least-squares against F^2. All non-hydrogen atoms were refined anisotropically. Except **2b**, hydrogen atoms at carbon atoms were placed at calculated positions and refined as riding atoms. Compound **2c** was a thin weakly diffracting needle, which resulted in low resolution, poor data/parameter ratio and low completeness; however, the structure was determined unambiguously. The crystal data and refinement parameters are presented in Table S1. CCDC 2153723 (**2a**), 2144693 (**2b**), 2153724 (**2c**), contain the supplementary crystallographic data for this paper.

Synthesis, NMR- and IR- data for 3,4,5-triaryl-1,2-diphosphaferrocene 2a-c

Starting materials: [FeCp(η^6-$C_6H_5CH_3$)][PF_6][13] and Na(diglyme)$_2$-3,4,5-triaryl-1,2-diphosphacyclopentadienides (**1a-c**)[14,15] were prepared according to literature procedures.

3,4,5-Triphenyl-1,2-diphosphaferrocene (2a): [FeCp(η^6-$C_6H_5CH_3$)][PF_6] (2.23 g, 6.23 mmol) was added to sodium 3,4,5-triphenyl-1,2-diphospholide (**1a**) (3.86 g, 6.23 mmol) which was previously dissolved in 25 ml diglyme and cooled to -80 °C. The reaction mixture was stirred at low temperature for a 3 h and then heated to 160 °C for an additional 3 h. Then the reaction mixture was cooled to room temperature, the solvent was evaporated and the remaining solid was dissolved in 30 ml toluene, passed through a layer of silica (4-5 cm), and the silica was additionally washed with toluene (3x 15 ml). After removal of the solvent **2a** was obtained as a reddish oil (2.05 g, 73% yield), which crystallized on standing.
^{1}H NMR ($CDCl_3$, δ, ppm): 4.59 (s, 5H, Cp), 7.08-7.22 (m, 15H, Ph).
$^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): -13.4 (s).
$^{13}C\{^1H\}$ ($CDCl_3$, δ, ppm, J, Hz): 75.6 (s, Cp), 108.1 (ps.t, $^2J_{CP} = 5.4$, P_2C_3), 114.5 (ps.t, $^1J_{CP} = 41.7$, P_2C_3), 126.3 (s, *p*-C in Ph), 126.8 (s, *p*-C in Ph), 127.3 (s, *m*-C in Ph), 130.9 (s, *o*-C in Ph), 132.3 (s, *o*-C in Ph), 137.2 (s, *ipso*-C in Ph), 141.0 (ps.t, $^2J_{CP} = 8.0$ Hz, *ipso*- C in Ph).
IR (KBr, cm^{-1}): 3078 (w), 3054 (w), 3022 (w), 2963 (w), 1596 (m), 1490 (s), 1442 (m), 1414 (w), 1261 (m), 1173 (w), 1156 (w), 1096 (m), 1076 (s), 1028 (s), 1007 (m), 910 (w), 825 (m), 790 (m), 755 (m), 729 (s), 695 (s), 653 (m), 581 (m), 559 (s), 478 (w), 451 (m), 424 (m).
Calculated for $C_{26}H_{20}FeP_2$ (M 450.2): C 69.33, H 4.44, Fe 12.44, P 13.77. Found: C 70.04, H 4.87, P 13.32.

3,4,5-Tris(*p*-methylphenyl)-1,2-diphosphaferrocene (2b): [FeCp(η^6-$C_6H_5CH_3$)][PF_6] (1.16 g, 3.26 mmol) was added to sodium 3,4,5-tris(*p*-methylphenyl)-1,2-diphospholide (**1b**) (2.16 g, 3.26 mmol) which was previously dissolved in 25 ml diglyme and cooled to -80 °C. The reaction mixture was stirred at low temperature for 3 h and then heated to 160 °C for an additional 3 h. Then the reaction mixture was cooled to room temperature, the solvent was evaporated and the remaining solid was dissolved in 30 ml toluene, passed through a layer of silica (4-5 cm), and the silica was additionally washed with toluene (3x 15 ml). After removal of the solvent **2b** was obtained as a reddish oil (1.25 g, 78% yield), which crystallized on standing.
^{1}H NMR ($CDCl_3$, δ, ppm): 2.20 (s, 9H, Me), 4.44 (s, 5H, Cp), 6.83 (d, 6H, Ph), 6.91 (d, 6H, Ph).
$^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): -15.4 (s).
$^{13}C\{^1H\}$ ($CDCl_3$, δ, ppm, J, Hz): 20.9 (s, Me), 75.4 (s, Cp), 107.6 (ps.t, $^2J_{PC} = 5.3$, P_2C_3), 114.3 (ps.t, $^1J_{PC} = 40.9$, P_2C_3), 128.0 (s, *p*-C in Ph), 130.7 (s, *m*-C in Ph), 132.1 (s, *m*-C in Ph), 134.1 (s, *o*-C in Ph), 135.8 (s, *o*-C in Ph), 136.2 (s, *ipso*-C in Ph), 138.2 (ps.t, $^2J_{PC} = 7.9$ Hz, *ipso*-C in Ph).
IR (KBr, cm^{-1}): 3082 (w), 3046 (w), 3023 (w), 2962 (w), 2918 (w), 2866 (w), 1899 (w), 1608 (w), 1511 (s), 1449 (m), 1415 (m), 1261 (s), 1181 (m), 1086 (br.), 1021 (s), 809 (s), 733 (m), 664 (w), 557 (m), 533 (w), 500 (m), 447 (m).
Calculated for $C_{29}H_{26}FeP_2$ (M 492.3): C 70.73, H 5.29, Fe 11.38, P 12.60. Found: C 71.23, H 5.87, P 12.34.

3,4,5-Tris(*p*-chlorophenyl)-1,2-diphosphaferrocene (2c): [FeCp(η^6-$C_6H_5CH_3$)][PF_6] (1.62 g, 4.52 mmol) was added to sodium 3,4,5-tris(*p*-chlorophenyl)-1,2-diphospholide (**1c**) (3.27 g, 4.52 mmol) which was previously dissolved in 25 ml diglyme and cooled to -80 °C. The reaction mixture was stirred at low temperature for 3 h and then heated to 160 °C for an additional 3 h. Then the reaction mixture was cooled to room temperature, the solvent was evaporated and the remaining solid was dissolved in 30 ml toluene, passed through a layer of silica (4-5 cm), and the silica was additionally washed with toluene (3x 15 ml). After removal of the solvent **2c** was obtained as a reddish oil (1.77 g, 71% yield), which crystallized on standing.

^{1}H NMR ($CDCl_3$, δ, ppm): 4.45 (s, 5H, Cp), 6.92 (d, 6H, Ph), 7.02 (d, 6H, Ph).

^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm): -11.4 (s).

^{13}C{^{1}H} ($CDCl_3$, δ, ppm, J, Hz): 75.7 (s, Cp), 106.8 (ps.t, $^2J_{PC}$ = 5.5, P_2C_3), 113.2 (ps.t, $^1J_{PC}$ = 41.7, P_2C_3), 127.7 (s, *p*-C in Ph), 128.0 (s, *p*-C in Ph), 131.9 (s, *m*-C in Ph), 132.6 (s, *m*-C in Ph), 133.2 (s, *o*-C in Ph), 133.4 (s, *o*-C in Ph), 135.3 (s, *ipso*-C in Ph), 139.2 (ps.t, $^2J_{PC}$ = 8.1 Hz, *ipso*-C in Ph).

IR (KBr, cm^{-1}): 3049 (w), 2946 (w), 2918 (w), 2857 (w), 1897 (w), 1590 (w), 1486 (s), 1397 (m), 1262 (w), 1173 (w), 1088 (s), 1013 (s), 962 (w), 935 (w), 829 (s), 815 (s), 744 (s), 721 (w), 699 (w), 655 (w), 649 (w), 557 (m), 501 (w), 513 (w), 478 (w), 451 (w).

Calculated for $C_{26}H_{17}Cl_3FeP_2$ (M 553.5): C 56.37, H 3.07, Cl 19.24, Fe 10.12, P 11.20. Found: C 56.43, H 3.18, P 11.14.

Fig. S1 Experimental (top, in CH_2Cl_2, c = 10^{-5}) and calculated (bottom, convoluted with a Lorentzian lineshape function fwhm = 0.25 eV) UV-Vis spectra of **2a** (black), **2b** (blue) and **2c** (red).

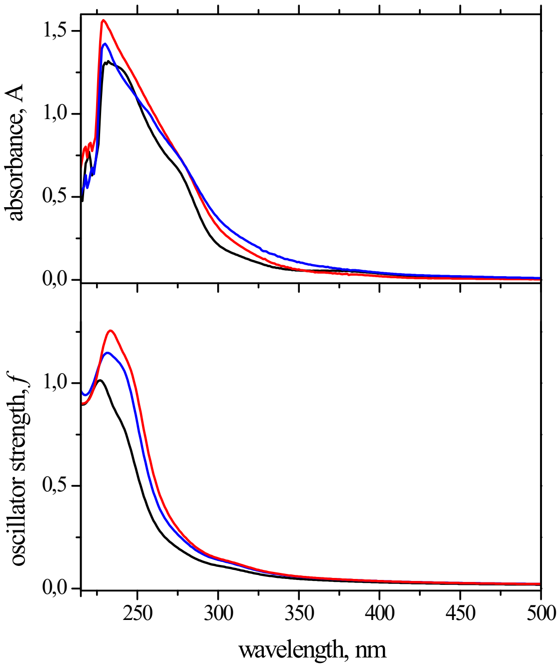

Table S1 Crystallographic data for the compounds **2a-c**

Compound	**2a**	**2b**	**2c**
Formula	$C_{26}H_{20}FeP_2$	$C_{29}H_{26}FeP_2$	$C_{26}H_{17}Cl_3FeP_2$
Formula weight (g mol^{-1})	450.21	492.29	553.53
Temperature (K)	150	130(2)	150
Wavelength (Å)	0.71073	0.71073	1.54178
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	Pn	P2_1/n	Cc
Unit cell dimensions (Å, º)	a = 10.732(1)	a = 7.8372(2)	a = 16.291(1)
	b = 8.8035(8)	b = 19.1823(5)	b = 18.523(1)
	c = 10.996(1)	c = 15.8804(4)	c = 7.7350(5)
	β = 97.154(2)	β = 91.495(2)	β = 96.554(4)
Volume (Å^3)	1030.8(2)	2386.6(1)	2318.8(3)
Z	2	4	4
d_{calc} (g cm^{-3})	1.450	1.370	1.586
μ (mm^{-1})	0.897	0.781	9.803
F(000)	464	1024	1120
Crystal size (mm^3)	0.234 x 0.125 x 0.112	0.20 x 0.20 x 0.02	0.321 x 0.036 x 0.033
θ range (º)	2.313 to 28.762	2.123 to 30.692	3.627 to 58.280
Index ranges	$-14 \leq h \leq 14$, $-11 \leq k \leq 11$, $-14 \leq l \leq 14$	$-11 \leq h \leq 11$, $-27 \leq k \leq 27$, $-22 \leq l \leq 22$	$-16 \leq h \leq 17$, $-19 \leq k \leq 19$, $-6 \leq l \leq 8$
Reflections collected	20691	45581	12427
Independent reflections	5328	6894	2493
Observed reflections	4758	4513	2416
R_{int}	0.0454	0.0803	0.0400
Completeness to θ_{full} (%)	100.0	100 % (28.29°)	89.1
Data / restraints / parameters	5328 / 2 / 262	6894 / 30 / 393	2493 / 2 / 289
Goodness-of-fit on F^2	1.024	1.006	1.057
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0296, wR^2 = 0.0558	R_1 = 0.0495, wR^2 = 0.0968	R_1 = 0.0261, wR^2 = 0.0669
R indices (all data)	R_1 = 0.0376, wR_2 = 0.0582	R_1 = 0.0956, wR_2 = 0.1134	R_1 = 0.0271, wR_2 = 0.0679
Absolute structure parameter	–0.003(7)	–	–0.018(5)
Largest diff. peak and hole (eÅ^{-3})	0.320 and -0.256	0.393 and -0.338	0.200 and -0.325

Table S2. Bond lengths [Å] and angles [°] for **2a**

Fe(1)-C(6)	2.057(3)
Fe(1)-C(5)	2.058(3)
Fe(1)-C(8)	2.058(3)
Fe(1)-C(4)	2.058(3)
Fe(1)-C(7)	2.058(3)
Fe(1)-C(1)	2.065(3)
Fe(1)-C(3)	2.067(3)
Fe(1)-C(2)	2.069(3)
Fe(1)-P(2)	2.3255(8)
Fe(1)-P(1)	2.3286(9)
P(1)-C(3)	1.783(3)
P(1)-P(2)	2.1297(11)
P(2)-C(1)	1.787(3)
C(6)-Fe(1)-C(5)	40.24(12)
C(6)-Fe(1)-C(8)	67.47(13)
C(5)-Fe(1)-C(8)	67.45(13)
C(6)-Fe(1)-C(4)	67.47(12)
C(5)-Fe(1)-C(4)	40.05(13)
C(8)-Fe(1)-C(4)	40.17(12)
C(6)-Fe(1)-C(7)	40.21(12)
C(5)-Fe(1)-C(7)	67.63(12)
C(8)-Fe(1)-C(7)	40.20(12)
C(4)-Fe(1)-C(7)	67.59(12)
C(6)-Fe(1)-C(1)	157.68(12)
C(5)-Fe(1)-C(1)	120.74(12)
C(8)-Fe(1)-C(1)	121.49(12)
C(4)-Fe(1)-C(1)	105.27(12)
C(7)-Fe(1)-C(1)	158.61(12)
C(6)-Fe(1)-C(3)	103.73(12)
C(5)-Fe(1)-C(3)	114.97(13)
C(8)-Fe(1)-C(3)	164.21(12)
C(4)-Fe(1)-C(3)	150.37(12)
C(7)-Fe(1)-C(3)	124.80(12)
C(1)-Fe(1)-C(3)	71.72(11)
C(6)-Fe(1)-C(2)	122.69(12)
C(5)-Fe(1)-C(2)	104.77(12)
C(8)-Fe(1)-C(2)	155.25(12)
C(4)-Fe(1)-C(2)	118.85(12)
C(7)-Fe(1)-C(2)	160.64(11)
C(1)-Fe(1)-C(2)	40.65(11)
C(3)-Fe(1)-C(2)	40.53(11)

C(6)-Fe(1)-P(2)	154.69(9)
C(5)-Fe(1)-P(2)	157.54(9)
C(8)-Fe(1)-P(2)	100.98(10)
C(4)-Fe(1)-P(2)	118.95(10)
C(7)-Fe(1)-P(2)	116.67(9)
C(1)-Fe(1)-P(2)	47.57(8)
C(3)-Fe(1)-P(2)	81.59(9)
C(2)-Fe(1)-P(2)	77.45(8)
C(6)-Fe(1)-P(1)	111.13(9)
C(5)-Fe(1)-P(1)	147.97(10)
C(8)-Fe(1)-P(1)	121.89(9)
C(4)-Fe(1)-P(1)	161.93(10)
C(7)-Fe(1)-P(1)	99.31(9)
C(1)-Fe(1)-P(1)	82.36(8)
C(3)-Fe(1)-P(1)	47.40(9)
C(2)-Fe(1)-P(1)	77.70(8)
P(2)-Fe(1)-P(1)	54.46(3)
C(3)-P(1)-P(2)	94.23(10)
C(3)-P(1)-Fe(1)	58.59(9)
P(2)-P(1)-Fe(1)	62.69(3)
C(1)-P(2)-P(1)	95.13(10)
C(1)-P(2)-Fe(1)	58.55(9)
P(1)-P(2)-Fe(1)	62.84(3)
C(2)-C(1)-P(2)	117.2(2)
C(9)-C(1)-P(2)	116.6(2)
C(2)-C(1)-Fe(1)	69.83(16)
C(9)-C(1)-Fe(1)	129.17(18)
P(2)-C(1)-Fe(1)	73.88(10)

Table S3. Torsion angles [°] for **2a**

P(2)-C(1)-C(9)-C(10)	-131.8(3)
P(2)-C(1)-C(9)-C(14)	43.5(3)
C(3)-C(2)-C(15)-C(20)	-124.1(3)
C(3)-C(2)-C(15)-C(16)	56.5(4)
P(1)-C(3)-C(21)-C(26)	-139.8(3)
P(1)-C(3)-C(21)-C(22)	37.6(3)

Table S4. Bond lengths [Å] and angles [°] for **2c**

Fe(1)-C(5)	2.038(6)
Fe(1)-C(4)	2.043(6)
Fe(1)-C(7)	2.054(6)
Fe(1)-C(6)	2.058(6)
Fe(1)-C(8)	2.059(6)
Fe(1)-C(3)	2.065(5)
Fe(1)-C(2)	2.070(5)
Fe(1)-C(1)	2.076(6)
Fe(1)-P(1)	2.3238(18)
Fe(1)-P(2)	2.3287(15)
P(1)-C(3)	1.792(5)
P(1)-P(2)	2.129(2)
P(2)-C(1)	1.788(5)
C(5)-Fe(1)-C(4)	40.5(3)
C(5)-Fe(1)-C(7)	67.4(3)
C(4)-Fe(1)-C(7)	67.7(3)
C(5)-Fe(1)-C(6)	40.0(3)
C(4)-Fe(1)-C(6)	67.6(3)
C(7)-Fe(1)-C(6)	40.0(2)
C(5)-Fe(1)-C(8)	67.5(2)
C(4)-Fe(1)-C(8)	40.3(3)
C(7)-Fe(1)-C(8)	40.0(3)
C(6)-Fe(1)-C(8)	67.2(2)
C(5)-Fe(1)-C(3)	122.7(2)
C(4)-Fe(1)-C(3)	159.2(2)
C(7)-Fe(1)-C(3)	122.2(2)
C(6)-Fe(1)-C(3)	107.2(2)
C(8)-Fe(1)-C(3)	158.3(2)
C(5)-Fe(1)-C(2)	106.4(2)
C(4)-Fe(1)-C(2)	123.8(2)
C(7)-Fe(1)-C(2)	155.7(2)
C(6)-Fe(1)-C(2)	120.2(2)
C(8)-Fe(1)-C(2)	161.5(2)
C(3)-Fe(1)-C(2)	39.8(2)
C(5)-Fe(1)-C(1)	115.0(2)
C(4)-Fe(1)-C(1)	102.9(2)
C(3)-Fe(1)-C(1)	71.3(2)
C(2)-Fe(1)-C(1)	40.7(2)
C(5)-Fe(1)-P(1)	158.5(2)
C(4)-Fe(1)-P(1)	152.86(18)
C(7)-Fe(1)-P(1)	100.36(19)
C(8)-Fe(1)-P(1)	115.16(19)

C(3)-Fe(1)-P(1)	47.74(14)
C(2)-Fe(1)-P(1)	77.27(16)
C(1)-Fe(1)-P(1)	81.96(17)
C(5)-Fe(1)-P(2)	146.9(2)
C(4)-Fe(1)-P(2)	109.47(18)
C(7)-Fe(1)-P(2)	121.14(16)
C(6)-Fe(1)-P(2)	161.10(18)
C(8)-Fe(1)-P(2)	98.16(17)
C(3)-Fe(1)-P(2)	81.88(14)
C(2)-Fe(1)-P(2)	77.51(14)
C(1)-Fe(1)-P(2)	47.48(14)
P(1)-Fe(1)-P(2)	54.46(5)
C(3)-P(1)-P(2)	94.40(19)
C(3)-P(1)-Fe(1)	58.54(18)
P(2)-P(1)-Fe(1)	62.89(6)
C(1)-P(2)-P(1)	94.8(2)
P(1)-P(2)-Fe(1)	62.65(6)
C(2)-C(1)-P(2)	117.0(4)
C(2)-C(1)-Fe(1)	69.4(3)
P(2)-C(1)-Fe(1)	73.7(2)

Table S5. Torsion angles [°] for **2c**

P(2)-C(1)-C(9)-C(14)	-39.6(7)
P(2)-C(1)-C(9)-C(10)	140.6(5)
C(3)-C(2)-C(15)-C(16)	-55.4(8)
C(3)-C(2)-C(15)-C(20)	120.2(6)
P(1)-C(3)-C(21)-C(22)	-49.4(7)
P(1)-C(3)-C(21)-C(26)	128.3(5)

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