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Synthesis of 3,4,5-tris(chlorophenyl)-1,2-diphosphaferrocenes and their electrochemical properties

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Abstract

A novel representative of sodium 3,4,5-triaryl-1,2-diphosphacyclopentadienide containing Cl-substituent in the *meta*- position of the aryl groups was obtained with a high yield based on the reaction of (1,2,3-triarylcyclopropenyl)tributylphosphonium bromide and sodium polyphosphides. Further reaction of sodium 3,4,5-tri(3-chlorophenyl)-1,2-diphosphacyclopentadienide with $[FeCp(\eta^6\text{-}C_6H_5CH_3)][PF_6]$ complex gives a new 3,4,5-tris(3-chlorophenyl)-1,2-diphosphaferrocene. The electrochemical properties of 3,4,5-tris(3-chlorophenyl)-1,2-diphosphaferrocene were studied and compared with 3,4,5-tris(4-chlorophenyl)-1,2-diphosphaferrocene. It was found that the position of the chlorine atom in the aryl fragment has a influence on the reduction potential of 1,2-diphosphaferrocenes, while the oxidation potentials do not change.

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Keywords

cyclopropenyl bromide, phosphonium salt, 1,2-diphosphacyclopentadienide anion, 1,2-diphosphaferrocene, phosphorus heterocycle, electrochemical properties

Introduction

Among the various heterometallocenes reported to date, phosphaferrocenes are by far the most investigated because of their structural and electronic features [1,2] and remain the objects of growing interest in the fields of coordination chemistry [3,4,5] and asymmetric catalysis [6,7]. Due to the sp^2-hybridization of the phosphorus atom, phosphaferrocenes are commonly regarded as phosphorus ligands with weaker σ-donor character than classical tertiary phosphines and stronger π-acceptor properties closer to phosphites $P(OR)_3$ [8,9]. Since the P-atom in phosphaferrocenes retains an electron lone pair, phosphaferrocenes were used as P-donor ligands [10,11,12] as well as nucleophilic catalysts [13,14]. Recently, pentaphosphaferrocene $[Cp^*Fe(\eta^5\text{-}P_5)]$ has been used as a mediator in the synthesis of asymmetric phosphines starting from white phosphorus [15]. Moreover, the presence of P-atom's lone pair opens the route to polynuclear complexes [16,17,18] and coordination polymers [19,20,21] with the mixed σ/π coordination mode, which is not typical for classical ferrocene species.

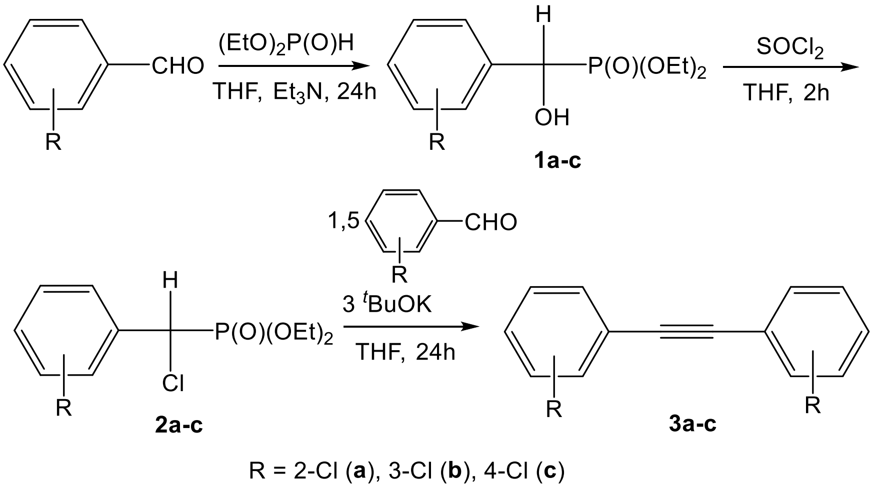
Various effective synthetic approaches were developed for 1-mono-[22,23,24], 1,2,3-tri-[25,26,27], 1,2,4-tri-[28,29,30], and pentaphosphaferrocenes [31,32,33], whereby their chemistry is most investigated and well represented at present time. In contrast, very limited data are available concerning 1,2-diphosphaferrocenes due to the absence of simple and effective routes to their synthesis [34,35,36]. Recently, we have reported a convenient synthesis of 3,4,5-triaryl-1,2-diphosphaferrocenes with various substituents at *para*-positions of aryl groups [37]. Based on this method, herein we report on the complete multistep synthesis of new sodium 3,4,5-tris(3-chlorophenyl)-1,2-diphosphacyclopentadienide and corresponding 1,2-diphosphaferrocene with *meta*-chlorophenyl substituent and the influence of the Cl-atom’s position in the aryl moiety on it`s electrochemical properties.

Results and Discussion

Synthesis of tris(chlorophenyl)cyclopropenyl bromides and their derivatives

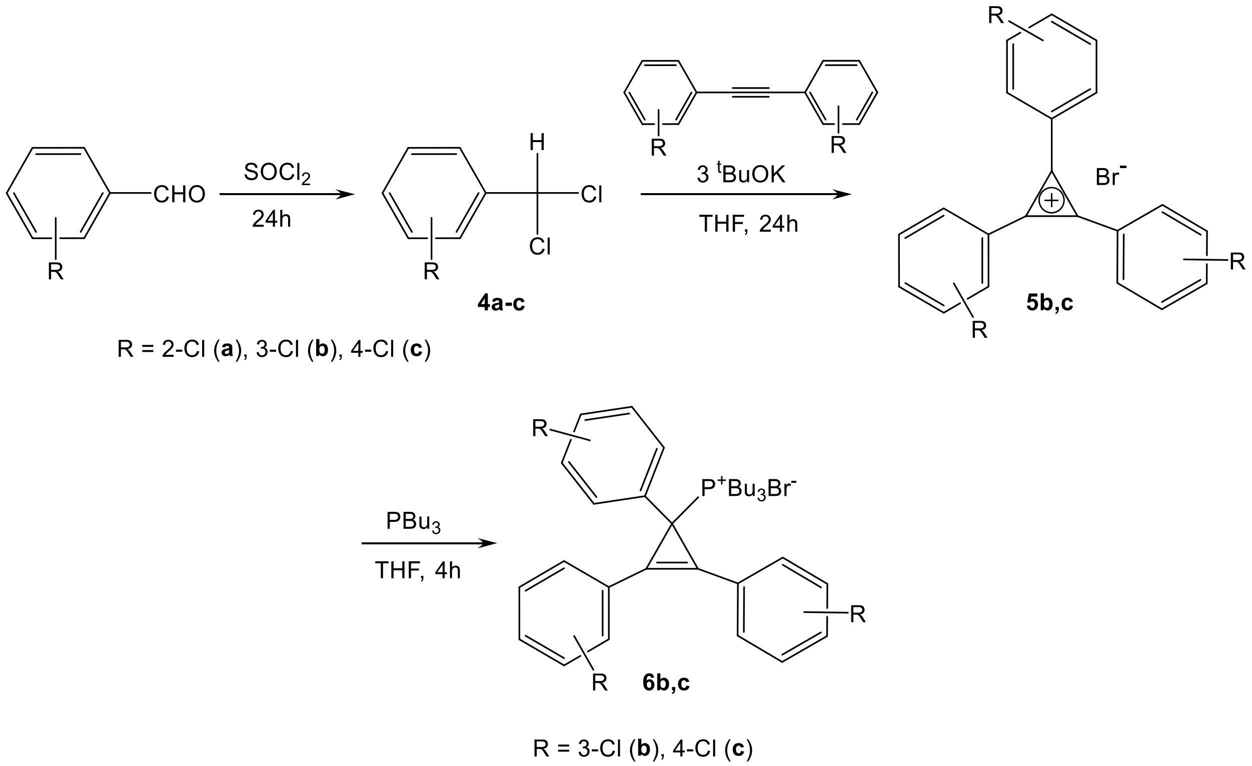
Cyclopropenium (cyclopropenylium) ions always attract attention of the synthetic chemists because of their unique combination of stability and reactivity [38,39,40]. Synthesis of corresponding 1,2,3-cyclopropenium bromides was realized by a classical approach **-** combination of the C_1 and C_2 building blocks, *i.e*. the addition of a carbene species to a triple bond of diarylacetylene, followed by treatment of the produced cyclopropene with HBr to convert it to the corresponding cyclopropenylium cation. Using this approach, tris(4-chlorophenyl)- and tris(3-chlorophenyl)cyclopropenylbromides have been prepared for the first time (Scheme 1). The advantage of this approach is the possibility of synthesis of substituted diarylacetylenes, the corresponding substituted benzal chlorides, and triarylcyclopropenyl bromides from one starting arylaldehyde.

Diethyl phosphite was allowed to react with appropriate substituted benzaldehydes in THF for 24 hours at 25 °C to afford diethyl hydroxy(aryl)methylphosphonates **1**, which were detected by ^{31}P NMR spectroscopy in THF (+21.6 ppm for **1a**, +21.0 ppm for **1b**, and +21.5 ppm for **1c**). Further, reaction mixtures with compounds **1** were treated with $SOCl_2$ for 1-2 h at 0 °C and converted to chloro-derivatives **2**. At the next step, compounds **2** and starting substituted benzaldehydes were subsequently treated with 2 eq. of potassium *tert*-butoxide ^{t}BuOK in THF for 12 h at room temperature to afford substituted diarylacetylenes **3**. Based on this reaction, the desired compounds **3** were prepared from 2-chloro-, 3-chloro- and 4-chlorophenylaldehydes with 10-53% yields in 3 steps (10.4% for **3a**, 48.0% for **3b**, 52.9% for **3c**) (Scheme 1). This method is an alternative way for different transition metal-catalyzed cross-coupling reactions broadly used for the preparation of different diarylacetylenes and rarely bis(chlorophenyll)acetylenes.



Scheme 1: Synthesis of bis(chlorophenyl)acetylenes **3**.

Next, starting substituted benzaldehydes were subsequently treated with an excess of $SOCl_2$ for 24 h at 25 °C. Corresponding substituted benzal chlorides **4** were distilled at reduced pressure to give pure compounds. In a final step, we used the abovementioned approach of combining the C_1 and C_2 building blocks and found that arylchlorocarbenes, generated from corrseponding benzal chlorides **4b**, **4c** under the action of potassium *tert*-butoxide, react with dichlorodiarylacetylenes **3b**, **3c** to form triarylcyclopropenylium salts **5b**, **5c** with 46-53% yields (Scheme 2). Unfortunately, it was not possible to synthesize tris(*o*-chlorophenyl)cyclopropenylium bromide **5a** using this method.



Scheme 2: Synthesis of 1,2,3-tris(chlorophenyl)cyclopropenylium bromides **5** and (1,2,3-tris(chlorophenyl)cyclopropenyl)tributylphosphonium bromides **6**.

The structures of **3-5** were confirmed by ^{1}H and ^{13}C NMR and IR spectroscopies as well as single-crystal X-ray diffraction for **5c** (Fig. 1a). The ^{13}C NMR signals of the three-membered-ring cationic carbons appeared at about +145 ppm; the ^{1}H NMR spectra of **5** are unremarkable and consistent with their formulation.

As a next step we synthesized a series of (1,2,3-triarylcyclopropenyl)tributylphosphonium bromides (**6**), containing Cl-substituent in the *meta*- and *para*-position of the aryl group, by reaction of 1,2,3-triarylcyclopropenylium bromides **5** with PBu_3 at 25 °C in THF in high yields (76-82%) (Scheme 2). The structures of **6** were confirmed by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopies. The ^{31}P{^{1}H} NMR spectra of tributylphosphonium bromides **6** contain a singlet at about +40 ppm, which is typical for phosphonium salts. The ^{13}C{^{1}H} NMR spectra consist of a doublet for the carbon atom C1 at about +20 ppm, which is characteristic for the sp^3-hybridized carbon atom, with a coupling constant $^1J_{CP} \approx 45$ Hz. Additionally, the structure of **6c** in crystals was confirmed by X-ray diffraction (Fig. 1b).

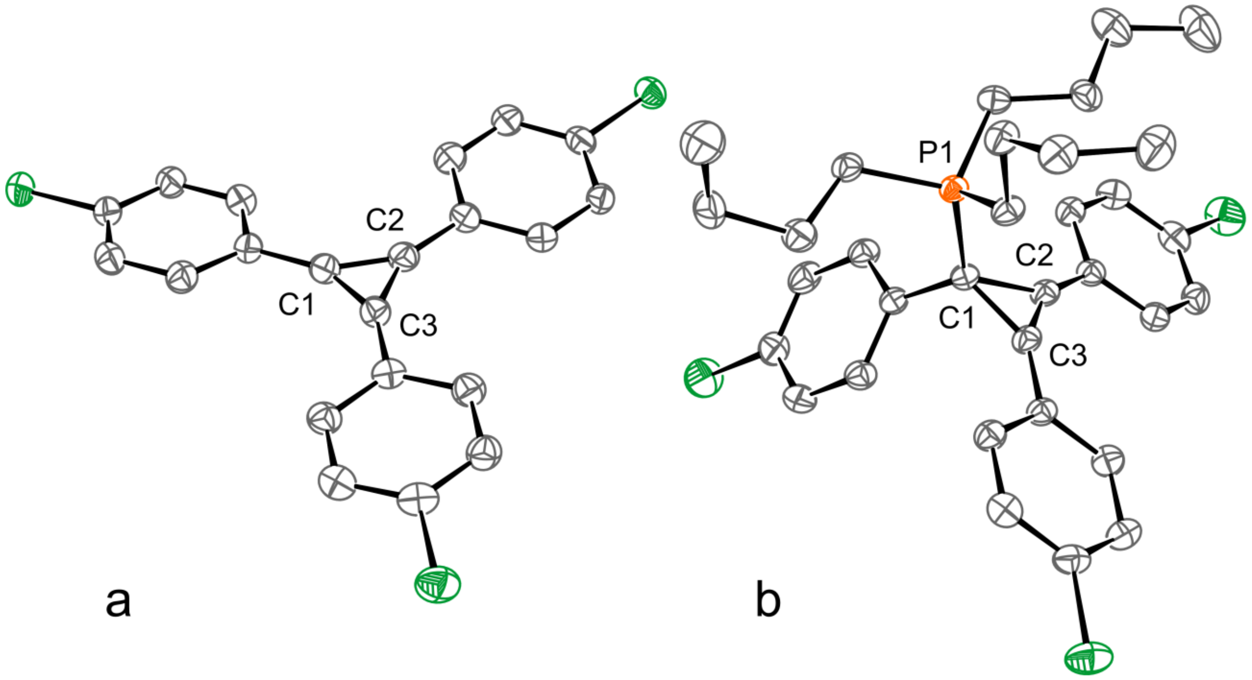
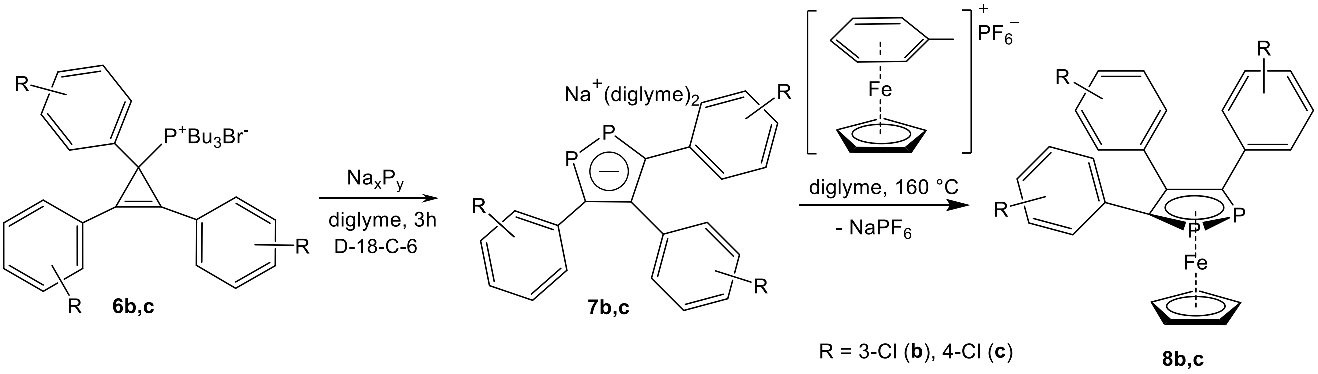


Figure 1. ORTEP representation for cations **5c** (a) and **6c** (b) at 50 % probability level according to SC XRD. Bromide anion and co-crystallized solvent molecules are omitted for clarity. In the case of **6c**, only one of two symmetry independent molecules is shown. Selected interatomic distances [Å]: C1–C2 1.387(7), C1–C3 1.372(7), C2–C3 1.380(7) for **5c**; C1–C2 1.521(5), C1–C3 1.521(5), C2–C3 1.298(5), P1–C1 1.837(3) for **6c**. Deposition numbers 2176393 (**5c**) and 2176394 (**6c**) contain the supplementary crystallographic data for this paper [41].

Synthesis, structure and electrochemical properties of 3,4,5-tris(*meta*-chlorophenyl)-1,2-diphosphaferrocene

The obtained phosphonium salts **6** were treated with a mixture of sodium polyphosphides Na_xP_y (obtained *in situ* from sodium metal Na and white phosphorus P_4 and containing mainly NaP_5 and Na_3P_7 [42]) resulting in sodium 3,4,5-tris(chlorophenyl)-1,2-diphospholides **7** in good yields (45-56%) (Scheme 3). This reaction allows a selective and controllable conversion of sodium polyphosphides Na_xP_y to 1,2-diphospholide anion, in which two new C−P bonds were selectively formed [43,44]. Obtained sodium 3,4,5-triaryl-1,2-diphospholides **7** were isolated in good purity from the reaction mixture by filtration and further washing with a mixture of THF/*n*-hexane. The $^{31}P\{^1H\}$ NMR spectra of **7** contain a singlet at about +200 ppm, which is typical for sodium 1,2-diphospholides ($^{31}P\{^1H\}$ in THF: +204 ppm for **7b** and +198 ppm for **7c**). The $^{13}C\{^1H\}$ NMR spectra of **7** show two multiplets at ca. +147 and +160 ppm for the heteroaromatic P_2C_3 ring backbone.



Scheme 3: Synthesis of 3,4,5-tris(chlorophenyl)-1,2-diphospholides **7** and 3,4,5-tris(chlorophenyl)-1,2-diphosphaferrocenes **8**.

Recently, we have reported a convenient method for the preparation of 1,2-diphosphaferrocenes [37] and 1,2,3-triphosphaferrocenes [25] with various substituents at *para*-positions of aryl groups. Using this approach, sodium 3,4,5-tris(3-chlorophenyl)-1,2-diphospholide **7b** was treated in a 1:1 ratio with $[FeCp(\eta^6\text{-}C_6H_5CH_3)][PF_6]$ at 160 °C in diglyme. Evaporation of diglyme at reduced pressure, extraction of the product with toluene followed by filtration through SiO_2 results in 3,4,5-tris(3-chlorophenyl)-1,2-diphosphaferrocene **8b** in good yield and high purity (Scheme 3).

The structure of 3,4,5-triaryl-1,2-diphosphaferrocene **8b** was confirmed by ^{31}P, ^1H, and

^{13}C NMR spectroscopies. $^{31}P\{^{1}H\}$ NMR spectra of **8b** show a singlet at ca. –10 ppm shifted upfield by ca. 210 ppm in comparison to the starting 1,2-diphospholide anion **7b**. In the ^{1}H NMR spectra, characteristic signals of the cyclopentadienyl ring (4.45 ppm) and ClC_6H_4 substituents (6.88-7.42 ppm) were observed. The $^{13}C\{^{1}H\}$ NMR spectra of **8b** show pseudotriplets at about 108 ppm and 114 ppm for the carbon atoms of P_2C_3 ring and a singlet at about 75 ppm for the cyclopentadienyl ring.

Quantum chemically two possible conformations of **8b** were considered (**I** and **II**, Fig. 2). Similar to previously reported **8c** [37] both **8b-I** and **8b-II** adopt almost eclipsed conformation during optimization. Computations predict slightly lower energy (1 kcal mol^{-1}) for conformation **8b-I** with Cl-atoms bent to the Fe-atom. According to the computations, **8b-I** is also slightly more energetically advantageous compared to **8c** with the same energy difference.

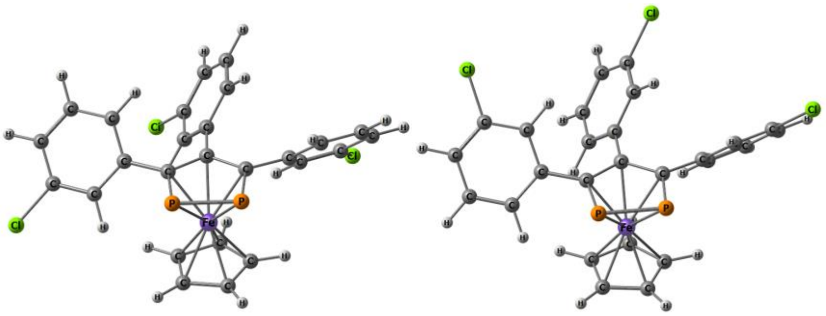


Figure 2. Considered conformations of **8b-I** (left) and **8b-II** (right).

The experimental UV-Vis spectra of **8b** and **8c** in CH_2Cl_2 are similar and contain the bands at about 280, 320, and 380 nm. The bands at 280 and 320 are more intensive in the spectrum of **8c**, which is in full agreement with quantum-chemical predictions (Fig. 3). According to the computations, **8b-I** and **8b-II** demonstrate almost the same absorption. The bands at ca. 250 and 280 nm are caused by π-π* transitions. The dominating transition contributing to the lowest-energy absorption (380 nm) is the one corresponding to a transition between HOMO-1 and LUMO+1 (Fig. 4). Both orbitals are localized mostly at [P_2C_3-Fe-Cp] moiety, the former is also contributed by atomic orbitals of the aryl ring in the 4-position. Similar to **8c** the atomic orbitals of Cl atoms in **8b** practically do not participate in the frontier orbitals, which explains the similarity of the low energy range of the experimental spectra.

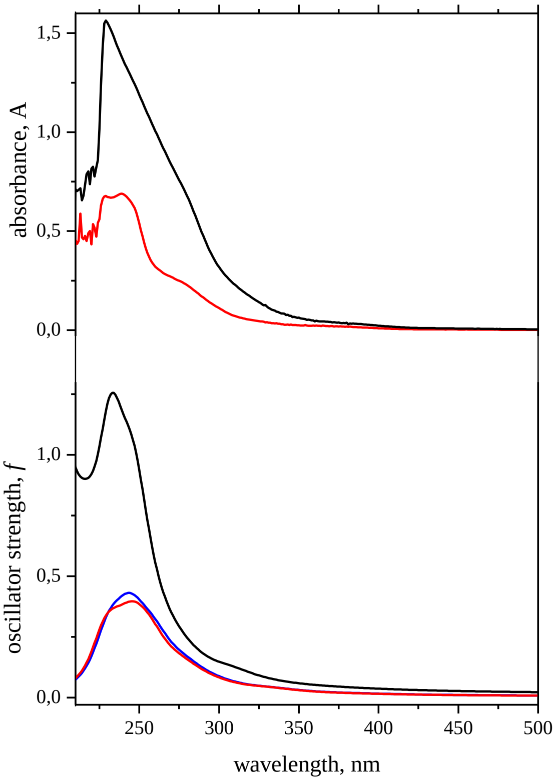


Figure 3. Top: experimental UV-Vis spectra of **8c** (black) and **8b** (red); bottom: broadened calculated UV-Vis spectra of **8c** (black) and **8b-I** (red) and **8b-II** (blue). Experimental UV-Vis spectra of **8c** republished with permission of Royal Society of Chemistry from [37] ("Synthesis, structure and electrochemical properties of 3,4,5-triaryl-1,2-diphosphaferocenes" by I. A. Bezkishko et al., Inorg. Chem. Front., vol. 9, Issue 11, © 2022); permission conveyed through Copyright Clearance Center, Inc. This content is not subject to CC BY 4.0.

HOMO-1 LUMO+1

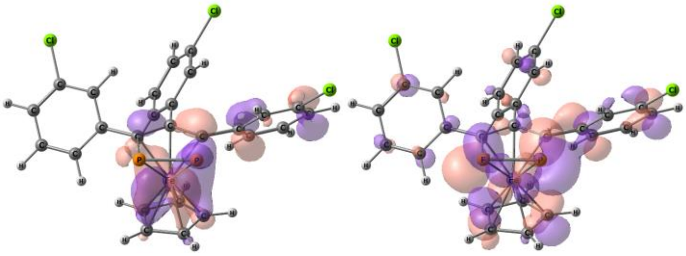


Figure 4. Frontier orbitals of **8b-II** contributing to absorption bands at ca. 380 nm.

The electrochemical properties of 1,2-diphosphaferrocene **8b** were studied by cyclic voltammetry and compared with data for **8c** (Figure 5, Table 1). During oxidation, there are no noticeable differences between **8b** and **8c**. The oxidation potentials of **8b** and **8c** are shifted to the positive region relative to pure ferrocene by 0.48–0.51 V. This, in turn, indicates that the chlorine atoms in the η^5-$P_2C_3R_3$ fragment do not significantly affect the HOMO energy of 1,2-diphosphaferrocenes **8**. The number of phosphorus atoms in cyclopentadiene has a much greater effect on the shifts of the Fe^{II}/Fe^{III} oxidation potential.

Table 1. Electrochemical data for redox properties of 3,4,5-triaryl-1,2-diphosphaferrocenes **8b** and **8c**.

Compound	E_{ox}^1 ,V vs. Fc/Fc$^+$	E_{red}^1, V	$^1E_{HOMO}$, eV	$^1E_{LUMO}$, eV	Gap, eV
Ferrocene [45]	0.48	-3.19 *	-4.79 *	-1.61 *	3.18 *
[FeCp(η^5-$P_2C_3R_3$)] (R = 3-Cl-C_6H_4) (**8b**)	0.96	-2.15	-5.28	-2.2	2.84
[FeCp(η^5-$P_2C_3R_3$)] (R = 4-Cl-C_6H_4) (**8c**)	1.01	-1.83	-5.36	-2.48	2.88

* Conditions: −50 °C, glassy carbon working electrode, Ag/AgCl ref. electrode, 0.5 mM concentration, Bu_4NBF_4, DMF, 100 mV s^{-1}.

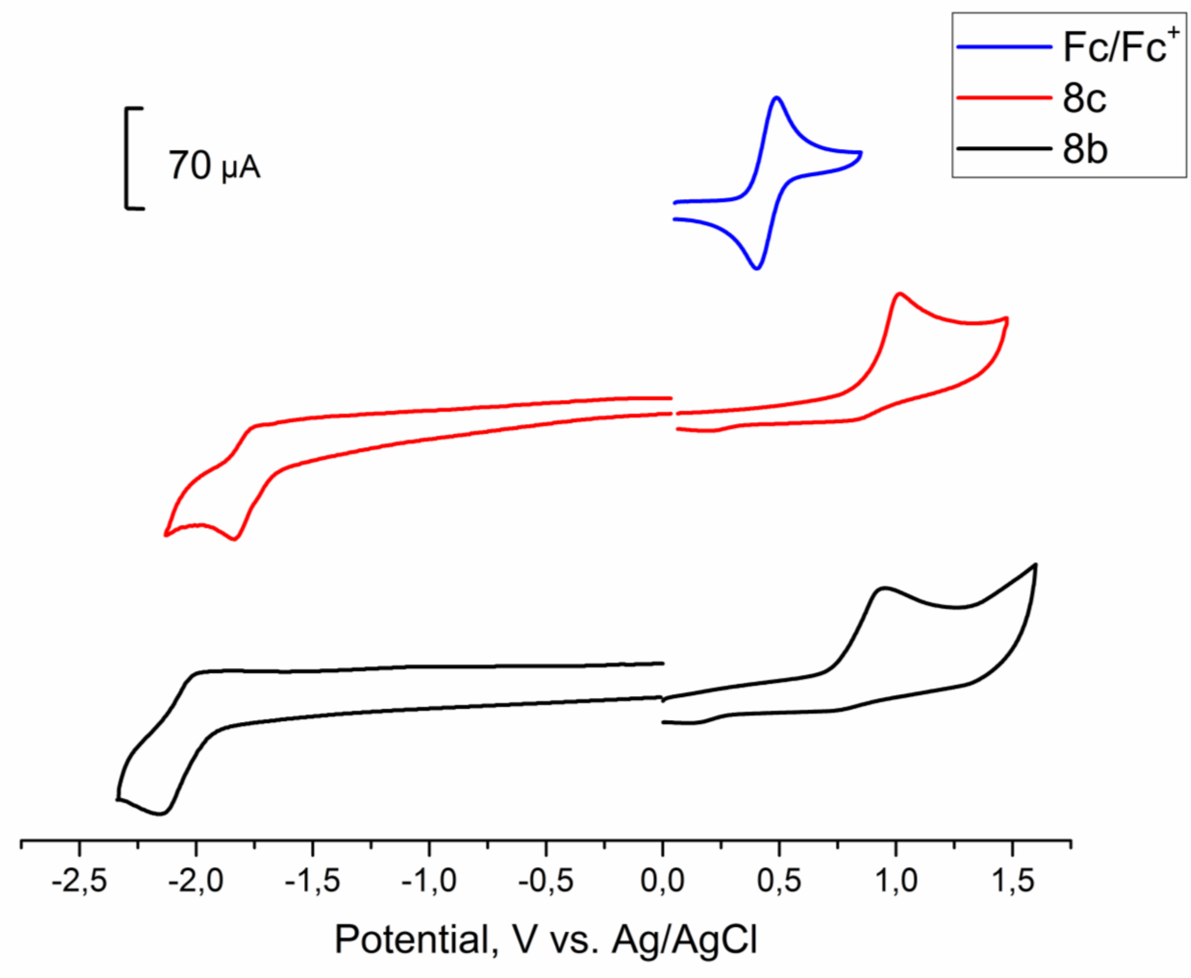


Figure 5. Cyclic voltammograms of 3,4,5-triaryl-1,2-diphosphaferrocenes **8b** and **8c** in CH_3CN on glassy carbon (GC) electrode (0.5 mM complex). The potentials vs. Ag/AgCl. Scan rate = 100 mV s^{-1}, room temperature. Cyclic voltammogram of **8c** republished with permission of Royal Society of Chemistry from [37] ("Synthesis, structure and electrochemical properties of 3,4,5-triaryl-1,2-diphosphaferocenes" by I. A. Bezkishko et al., Inorg. Chem. Front., vol. 9, Issue 11, © 2022); permission conveyed through Copyright Clearance Center, Inc. This content is not subject to CC BY 4.0.

In the case of reduction, the electrochemical picture changes more noticeable, since the contribution to LUMO comes from cyclopentadiene fragments. For 1,2-diphosphaferrocene **8b** the reduction potential is shifted by 0.33 V to a more negative region compared to **8c**.

Conclusions

In summary, a series of bis(chlorophenyl)acetylenes **3**, substituted benzal chlorides **4**, and tris(chlorophenyl)cyclopropenylium bromides **5** were synthesized starting from corresponding chloro-substituted benzaldehydes. We found that the reaction of (1,2,3-tris(chlorophenylcyclopropenyl)tributylphosphonium bromides **6** with sodium polyphosphides could be successfully used for the preparation of sodium 3,4,5-tris(chlorophenyl)-1,2-diphosphacyclopentadienides **7**. A facile synthesis of 3,4,5-tris(3-chlorophenyl)-1,2-diphosphaferrocene **8b** from sodium 3,4,5-tris(3-chlorophenyl)-1,2-diphosphacyclopentadienide **7b** and [FeCp(η^6-$C_6H_5CH_3$)][PF_6] is described. The structure of **8b** was studied from experimental (NMR, UV-spectra, and electrochemical studies) and theoretical points of view. The *meta*- / *para*-position of the Cl-atoms in the aryl fragment does not significantly effect on oxidation potentials of 1,2-diphosphaferrocenes **8**, while the reduction potential of **8b** is shifted by 0.33 V to a more negative region compared to **8c**.

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Supporting Information

Supporting Information File 1:

Experimental procedures, characterization data.

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