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Electrochemical arylation of iron and cobalt in metalloporphyrins with diphenyliodonium salts

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A new method for the electrochemical arylation of metalloporphyrins with diphenyliodonium salts yielding compounds with metal–phenyl σ-bonds has been proposed.

The activation of chemical reactions by electrochemical electron transfer is a multipurpose method for performing processes that require the generation of highly reactive species (cations, anions or radicals) or the formation of labile metal complexes.

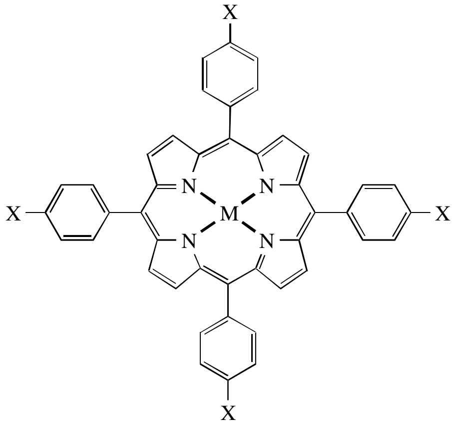
The synthesis of organometallic compounds containing metal–carbon (*sp*^{2}) σ-bonds belongs to reactions that require the electrochemical activation of an organic substrate in the presence of a metal complex.

Recently, a new electrochemical method for Co arylation in cobalt chelates with iodonium salts has been proposed in our laboratory.[1]

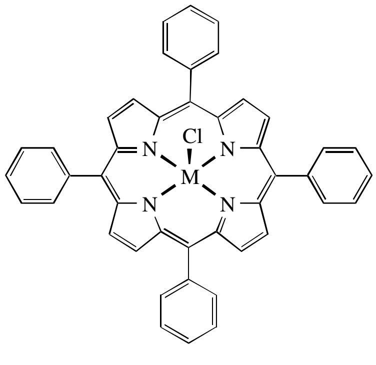
In this work, we studied the electrochemical arylation of iron, cobalt and nickel porphyrins with diphenyliodonium salts. The substrates were the porphyrin complexes of Group VIII elements (Fe, Co and Ni) because many naturally occurring metal complexes contain these elements (*e.g.*, hemoglobin, myoglobin and vitamin B_{12}).

Thus, the modification of porphyrins and similar N-containing macrocyclic complexes is of great interest from the standpoints of the synthesis of new compounds and the electrochemical modeling of naturally occurring processes.

The test porphyrin complexes are shown in Figure 1.



M(TPP) (M = Co, Ni; X = H)
Co(TMPP) (M = Co; X = OMe)



Co(TPP)Cl (M = Co)
Fe(TPP)Cl (M = Fe)

Figure 1

Diphenyliodonium salts were used as arylating agents. Their electrochemical reduction allows the generation of phenyl radicals at a low cathodic potential[2] (–1.05 V *vs.* Fc/Fc$^+$).[†] These radicals can react with paramagnetic transition-metal complexes to form compounds containing metal–phenyl σ-bonds:

$$Ph_2I^+BF_4^- + e \rightarrow Ph\cdot + PhI + BF_4^-$$

$$Ph\cdot + (Por)M \rightarrow (Por)MPh;\ Por = TPP,\ TMPP$$

The experiments were carried out in a two-compartment electrochemical cell under deaerated conditions at the reduction potential of diphenyliodonium ion.

The phenyl group can be introduced into metal porphyrins *via* the following three paths: (1) metal–phenyl σ-bond formation; (2) formation of N-phenylated porphyrins;[3–7] and (3) meso- or β-attack on the porphyrin macrocycle by a phenyl-containing organometallic reagent.[8–10]

Path 3 is known to proceed *via* the nucleophilic addition of PhLi to the macrocyclic ligand of the metalloporphyrin, and it is inherent mainly to Ni^{II} porphyrins.[8] The experimental conditions of our electrochemical process are strongly different from those for nucleophilic addition because the formation of the phenyl anion is highly improbable, that is why the possibility of such process in our case is very low.

Path 2 (the migration of a phenyl group from the metal to a nitrogen atom of the porphyrin ring) usually occurs under oxidative conditions (*e.g.*, $CCl_3COOH/CH_2Cl_2/O_2$)[3,4] or in electrochemical oxidation.[6,7] Our experiments were performed under reductive conditions; therefore, the migration of the phenyl group to the nitrogen atom seems unlikely. Moreover, porphyrin derivatives with a phenyl group attached to the metal or nitrogen atom can be easily distinguished using UV-VIS spectroscopy or cyclic voltammetry.[4,11,12] Soret band in case of PhFeTPP is much less red-shifted (422 nm, THF) in comparison with the initial FeTPPCl than in case of *N*-PhFeTPP (454 nm, THF).[11] In the case of CoTPP, the situation is the same.[4] The rest bands for PhMTPP and *N*-PhMTPP have also different wavelengths, and they can be easily distinguished.[4,11,12,14]

The monitoring of the reaction was performed using cyclic voltammetry (CVA) and electronic spectroscopy. The formation of an M–phenyl σ-bond in metalloporphyrins results in the appearance of reduction peaks at –1.85 V (PhCoTPP, PhCoTMPP[4,6]) and at –1.17 V (PhFeTPP[13]) [Pt, 0.05 M $Bu_4N^+BF_4^-$, DMF, *vs.* Fc/Fc$^+$], which are characteristic of arylated products containing M–phenyl σ-bonds. Besides, in the electronic spectra of the products, the Soret band is red-shifted with respect to that for initial metalloporphyrins. The wavelengths observed (430 nm for PhCoTPP, DMF and 422 nm for PhFeTPP, DMF) are consistent with the published values.[4,13]

These data allow us to conclude that the electrochemical process results in the formation of an M–phenyl σ-bond.

[†] Porphyrin complexes of Co^{II} and Fe^{II} were not reduced at this potential; Co^{III} and Fe^{III} porphyrins are reduced to Co^{II} and Fe^{II} species at –1.05 V *vs.* Fc/Fc$^+$.

Note that the reaction can be performed with both Co^{II} and Co^{III} porphyrins. In the latter case, the reduction of CoTPPCl to CoTPP occurs at the potential of diphenyliodonium salt reduction. Hence, the formation of phenyl radicals and paramagnetic CoTPP species takes place simultaneously. Thus created active species react with each other *in situ*.

$$\mathrm{Ph_2I^+BF_4^- + e \xrightarrow{-1.05\ V} Ph\cdot + PhI + BF_4^-}$$
$$\mathrm{CoTPPCl + e \xrightarrow{-0.78\ V} CoTPP + Cl^-}$$
$$\mathrm{CoTPP + Ph\cdot \longrightarrow \cdot PhCoTPP}$$

For iron porphyrins, the reaction proceeds *via* the same pathway.

To confirm the formation of porphyrins containing M–Ph σ-bonds in electrochemically activated reactions a non-electrochemical approach was also applied to the synthesis of arylated complexes. The reactions of Co^{III} and Fe^{III} porphyrins with PhLi[4] and PhMgBr,[14] respectively, were used:

$$\mathrm{M(TPP)Cl + M'Ph \longrightarrow PhM(TPP) + M'Cl}$$
$$\mathrm{M = Co, M' = Li;\ M = Fe, M' = MgBr}$$

The oxidation and reduction peak potentials, as well as spectral data, for the products of both electrochemical and chemical syntheses coincided completely.

The electrochemically activated reaction of equimolar amounts of the starting porphyrin complex and $Ph_2I^+BF_4^-$ leads to the almost complete consumption of diphenyliodonium tetrafluoroborate. However, a portion of the initial porphyrin remained unreacted. Thus, a part of the electrochemically generated phenyl radicals was adsorbed on the graphite electrode, entered competitive reactions, or was further reduced at the electrode. These competitive processes are responsible for a low current efficiency (15%) for the target reaction, as well as for the moderate yield of the arylated product (35%).

In this context, the question is how to decrease the absolute value of the electrolysis potential and to remove the reaction from the electrode surface. To solve this problem, we used homogeneous redox catalysis with 1,5-dinitroanthraquinone-9,10 as a mediator (A). The addition of the mediator decreased the absolute value of the electrolysis potential from –1.05 V to –0.9 V (*vs*. Fc/Fc+) and removed the reaction from the electrode surface to the bulk of the solution, thus increasing the yield of arylated complexes (up to 62%) and the current efficiency for the target process (20%).

$$\mathrm{A + e \xrightarrow{electrode} A^{\cdot -}}$$
$$\mathrm{Ph_2I^+BF_4^- + A^{\cdot -} \xrightarrow{solution} Ph\cdot + PhI + BF_4^- + A}$$
$$\mathrm{Ph\cdot + CoTMPP \xrightarrow{solution} PhCoTMPP}$$

Unfortunately, we failed to perform the electrochemical arylation of nickel porphyrins with diphenyliodonium salts either at the potential of $Ph_2I^+BF_4^-$ reduction or at the potential of the fist reduction peak of NiTPP (–1.75 V *vs*. Fc/Fc+). This is due to the fact that an additional electron is located on the porphyrin ligand,[15] and the formation of a paramagnetic Ni^I complex does not occur.

Thus, we have demonstrated that the electrochemical arylation of cobalt and iron porphyrins with diphenyliodonium salts results in the formation of metal–aryl σ-bonds. The proposed method possesses significant advantages as compared with the electrochemical arylation[13] of FeTPPCl using p-NC-C_4H_6I. The use of a diphenyliodonium salt as a source of aryl radicals allows us to reduce the absolute value of the reduction potential to almost 1.3 V with respect to iodobenzene. This considerably decreases the contribution of side processes and increases the selectivity of the reaction. The iodonium method allowed us to use metalloporphyrins that contain substituents sensitive to Grignard reagents in arylation reactions. Thus, it can compete with well-known[4,14,16] non-electrochemical routes of the synthesis of complexes containing metal–aryl σ-bonds, in particular those involving organometallics.

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References

1 T. V. Magdesieva, D. N. Kravchuk and K. P. Butin, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 83 (*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 85).

2 F. M. Beringer and R. A. Falk, *J. Chem. Soc.*, 1964, 4442.

3 H. J. Callot and F. Metz, *J. Chem. Soc., Chem. Commun.*, 1982, 947.

4 H. J. Callot, R. Cromer, A. Louati and M. Gross, *Nouv. J. Chim.*, 1984, **8**, 765.

5 R. C. Haddon, L. E. Brus and K. Raghavachari, *Chem. Phys. Lett.*, 1986, **125**, 459.

6 H. J. Callot, F. Metz and R. Cromer, *Nouv. J. Chim.*, 1984, **8**, 759.

7 D. Dolphin, D. J. Halko and E. Johnson, *Inorg. Chem.*, 1981, **20**, 4348.

8 M. O. Senge, W. W. Kalisch and I. Bischoff, *Chem. Eur. J.*, 2000, **15**, 2721.

9 B. Krattinger and H. J. Callot, *Tetrahedron Lett.*, 1998, **39**, 1165.

10 X. Feng and M. O. Senge, *J. Chem. Soc., Perkin Trans. 1*, 2001, 1030.

11 D. Lancon, P. Cocolios, R. Guilard and K. M. Kadish, *J. Am. Chem. Soc.*, 1984, **106**, 4472.

12 D. Kuila, A. B. Kopelove and D. K. Lavallee, *Inorg. Chem.*, 1985, **24**, 1443.

13 D. Lexa and J. M. Saveant, *J. Am. Chem. Soc.*, 1982, **104**, 3503.

14 P. R. Ortiz de Montellano, K. L. Kunze and O. Augusto, *J. Am. Chem. Soc.*, 1982, **104**, 3545.

15 M. V. Renner and J. Fajer, *J. Biol. Inorg. Chem.*, 2001, **6**, 823.

16 H. J. Callot and E. Shaeffer, *J. Organomet. Chem.*, 1980, **193**, 111.

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