Reviews

Ligand oxidation as a method for intramolecular activation of metal complexes

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The results of investigations of organometallic and coordination compounds whose ligands contain redox fragments based on 2,6-di-*tert*-butylphenol and linked to the metal by various coordinating groups are summarized. The redox properties of σ-aryl, π- and σ-allyl complexes, β-diketonates, hydrazides, hydroxamates, glyoximates, and metalloporphyrins and metallophthalocyanines are considered. The possibility of changing the reactivity of organometallic and coordination compounds by changing the magnetic state due to oxidation of the redox-active phenolic group in the ligand is demonstrated. It is proposed to use ligand oxidation as a method for intramolecular activation of metal complexes.

Key words: sterically hindered phenols, metal complexes, phenoxyl radicals, ESR, intramolecular activation.

Introduction

Organometallic and coordination chemistry is faced with the problem of selective activation of compounds. Activated metal-complex intermediates play a key role in the assembly of new molecules, in the design of new-generation materials for molecular electronics, in the processes induced by ionizing radiation, in the photoinduced electron transfer, in redox and photo catalysis, and in Chemical Vapor Deposition (CVD) processes. Chemical activation of the complex can be attained by intermolecular interaction with another reagent; in the limiting case, this is accompanied by bond cleavage and the change in the complex structure and results, for example, in the formation of a new reactive species with coordinationally unsaturated metal atom.[1] Yet another way of activation is the change in the electronic structure of the metal complex, which occurs by an intramolecular mechanism. One of these methods is preliminary change in the redox state of the molecule, for example, single-electron oxidation or reduction that does not cause the destruction of the complex but induces intramolecular transformation[2—6] or intramolecular electron transfer (IET).[7—10]

Intramolecular electron transfer has been studied in detail for multicomponent biological systems[6,11,12] but much less studied for simple chemical objects.

In recent years, the intermolecular (outer-sphere) and intramolecular (inner-sphere) electron transfer in metal complex systems has received enhanced attention (see, for example, a monograph[2]). This is largely due to the development of supramolecular chemistry and mo-

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lecular electronics,[2,5,13] in which these processes are important as expedients of molecular design. From this standpoint, compounds with two or more redox-active centers that can undergo effective electronic interaction are of interest. Primary attention is devoted to bi- and polynuclear metal complexes containing, as a rule, conductive linking bridges of the organic nature (L) and inorganic or organic ligands (L′, L″). Binuclear compounds of the general formula $L'M^1(L)M^2L''$ (**A**) can also be regarded as elementary units of polynuclear systems.

This research has been greatly stimulated by the publication of the results of investigation of the Kreitz—Taube ion $[(NH_3)_5Ru^{III}(pyz)Ru^{II}(NH_3)_5]^{5+}$ (pyz is pyrazine) and its numerous analogs[14—16] as well as bisferrocenes differing in both the linking groups (L) and the substituents in the cyclopentadienyl rings.[7,17,18] In type **A** models, the redox centers are represented by metal atoms able to change the oxidation state. In this case, complete electron transfer between M^1 and M^2 ($M^1 = M^2$ or $M^1 \neq M^2$) takes place by an intramolecular mechanism.

Yet another possibility of creating systems with strong intramolecular electronic and magnetic exchange interaction is generation of mononuclear metal complexes with reduced (radical anion) and oxidized (radical cation) forms of organic ligands (**B**, **C**):[2,19]

$$\underset{\mathbf{B}}{(L^{\bullet -})M} \xleftarrow{+e} LM \xrightarrow{-e} \underset{\mathbf{C}}{(L^{\bullet +})M}$$

For example, *o*-semiquinone complexes,[20—23] porphyrins,[24—28] and phthalocyanines[25,29—33] were found to be convenient as regards the formation of thermodynamically stable radical-ion forms of ligands.

Structures **B** and **C** contain (in the simplest case) two redox-active centers, namely, the paramagnetic ligand carrying a charge and a metal ion capable of changing the oxidation state. The system paramagnetism is retained due to the organic moiety of the molecule. In the case of species containing a metal ion with an odd number of electrons, antiferromagnetic interactions arise. However, in this case, intramolecular effects are not always accompanied by complete electron transfer in the metal—ligand pair but can occur as a substantial mutual effect of the two redox centers, which influences the overall reactivity and the physicochemical properties of the complexes.

One more line of research is related to the use of a free-radical organic fragment introduced in the ligand environment, R•(L)M (**D**), as the second active center in the complex (apart from the metal ion).

These systems have been studied comprehensively in relation to metal complexes with nitroxides.[34—37] Complexes of this type are formed when the metal atom is bound to the lone electron pair of the nitroxide nitrogen atom, or when nitroxides are introduced in the coordinating group of the ligand. In this case, either IET takes place[38] or the effects of long-range interactions between the spins of the unpaired electrons of the organic radical and the metal ion are manifested.[34]

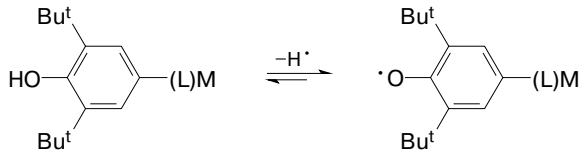
Despite the functional similarity of structures **A—D**, they are prepared in different ways. For example, in type **A** models, the IET is, most often, a consequence of thermal or photochemical activation; species **B** and **C** are normally generated by an electrochemical method, while compounds **D** are formed during the synthesis using knowingly stable radical reagents.

In studies of real chemical processes, interest is aroused by the systems that can be used as reagents thermodynamically stable under normal conditions but undergo subsequently chemical activation giving rise, for example, to type **D** structures, which results in an intramolecular rearrangement of the electronic system of the complexes.

Sterically hindered phenols as redox fragments of ligands in metal complexes

Previously, we proposed[39] to use sterically hindered 2,6-di-*tert*-butylphenols converted into stable phenoxyl radicals upon oxidation as functional redox-active groups introduced in the coordination sphere of complexes (Scheme 1).

Scheme 1



L is the coordinating group, M is metal and its environment

Advanced synthetic methods allow the introduction of sterically hindered phenols as ligands in complexes with different types of the ligand—metal bond.[40] The main types of metal complexes based on 2,6-di-*tert*-butylphenols and characteristics of the resulting radical products have been reported in a review.[41]

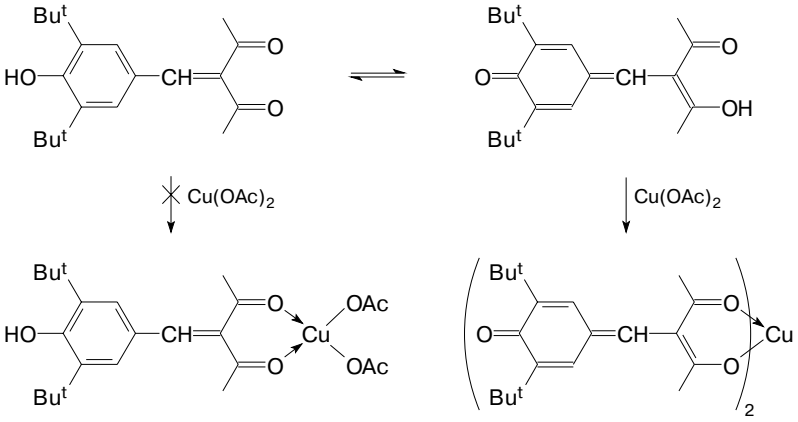
Using these compounds, one can perform a comparative analysis of the structure, properties, and reactivity of complexes with the radical ligand R•(L)M and the corresponding diamagnetic compounds R(L)M (R and R• are the 2,6-di-*tert*-butylphenol and 2,6-di-*tert*-butylphenoxyl radical fragments).

This brings about several fundamental questions:

(1) Is it possible to carry out selective oxidation of the organic moiety of the molecule with generation of the paramagnetic fragment, phenoxyl radical, as a ligand fragment, without violating the coordination structure of the complex, *i.e.*, would the complex undergo oxidative destruction?

(2) What are the factors determining the thermodynamic and kinetic stability of metal-containing radicals

Scheme 2



and the reversibility of oxidation processes and what are the conditions under which the mutual effect of the radical ligand and the metal atom can be detected?

(3) How can the redox processes involving this type of complex be controlled for attaining intramolecular activation of various reaction centers in the molecule?

Regarding the first question, the available experimental data allow one to claim that in the vast majority of cases, it is possible to carry out reversible oxidation of the ligand and to detect the resulting radical species by ESR spectroscopy. Virtually none of the complexes in question undergoes destruction at a temperature of ≤20 °C.

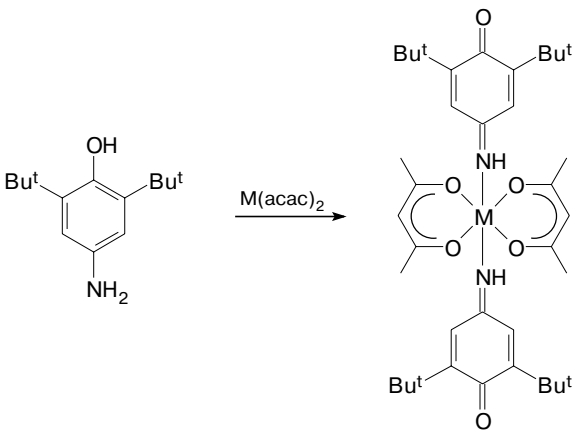
However, in some cases, the synthesis of the starting diamagnetic phenolic complexes is faced with difficulties. Thus the attempt to prepare copper β-diketonates from 3-(3′,5′-di-*tert*-butyl-4′-hydroxybenzylidene)pentane-2,4-dione showed[42] that the formation of the complex with the enolyzed diketone is preferred (Scheme 2).

Due to the ease of oxidation of 3,5-di-*tert*-butyl-4-hydroxyaniline, in the presence of Co^{II} and Ni^{II} acetylacetonates, quinonimine complexes are formed (Scheme 3), whose structure was confirmed by X-ray diffraction analysis.[43]

A similar process has been observed in the synthesis of Co^{II} and Ni^{II} phthalocyanines from 4-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyalamino)-3,5,6-trichlorophthalodinitrile.[44] This reaction can follow two pathways: either the initial substrate undergoes oxidation to give a quinoid product (pathway *a*) or the oxidation of the phenolic groups at the periphery of the macroligand is preceded by complex formation (pathway *b*) (Scheme 4).

Despite the absence of phenolic groups in the above complexes, these compounds can still be of interest for performing the processes of ligand reduction (preparation of type **B** complexes) because quinoid derivatives are effective electron acceptors. In the synthesis of numerous complexes with phenols, it is possible not only to introduce a phenolic fragment into the ligand environment but also to perform selective oxidation of the

Scheme 3

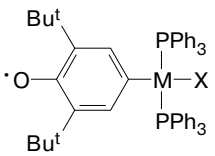


M = Co, Ni

phenol, to generate paramagnetic complexes, and to study intramolecular transformations.

Intramolecular transformations in organometallic and coordination compounds containing radical fragments in the ligands

Paramagnetic σ-aryl Pt^{II} and Pd^{II} compounds with a C—M bond in the *para*-position of the phenoxyl ring (**1a,b**) are fairly stable;[45] the half-life ($\tau_{1/2}$) of these compounds in solution is several days.

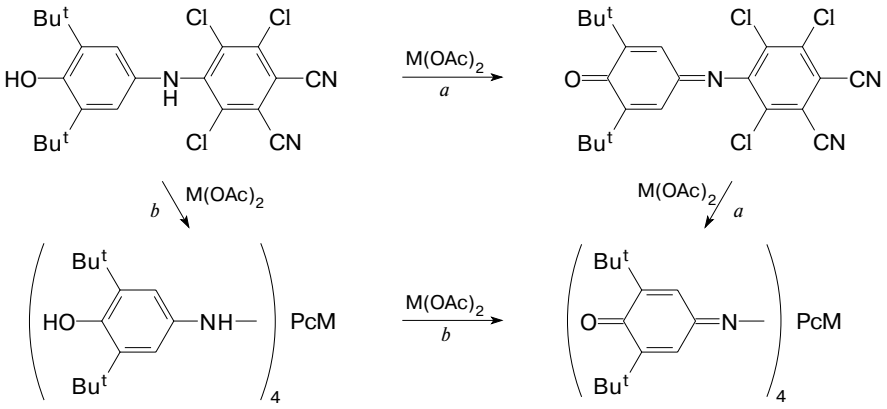


1a,b

1a: M = Pt, **1b:** M = Pd; X = Cl, Br, I

The reason for such a high stability of compounds **1a,b** lies in shielding of the reaction center

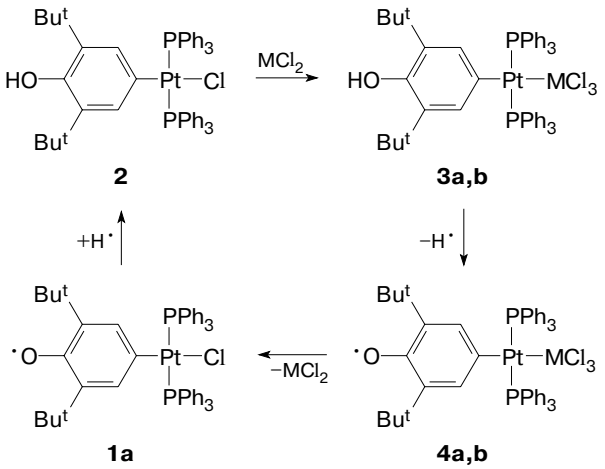
Scheme 4



M = Co, Ni; Pc is dodecachlorophthalocyaninato dianion

(*para*-position) and substantial involvement of metal d-electrons in the distribution of the spin density of the unpaired electron, which is confirmed by the HFC constants in the ESR spectra (Table 1). However, the introduction of a second metal atom in the organometallic group of the initial phenolic complex **2** (compounds **3a,b**) gives rise to different in kind properties of radicals **4a,b** [46] (Scheme 5).

Scheme 5

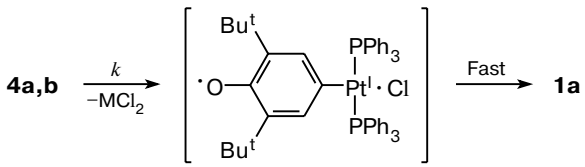


a: M = Sn, **b:** M = Ge

The pronounced decrease in the HFC constants of the unpaired electron with the ^{195}Pt nucleus ($\Delta a_{Pt} \approx 2$ mT) with respect to those for **1a** and the presence of the HFC with the $^{117/119}Sn$ nucleus (**4a**) (see Table 1) implies that some spin density has been transferred from the Pt atom to the Sn and Ge atoms by the spin-polarization mechanism, which is due to the π-acceptor properties of the $SnCl_3$ and $GeCl_3$ groups and to the ability of the Pt atom to transfer electron density (transmission effect).

The intramolecular electron changes are reflected in the kinetic and thermodynamic stability of paramagnetic species **4a,b**. They substantially differ in stability from radical **1a** and from diamagnetic precursors **3a,b**; the $\tau_{1/2}$ value in solutions amounts to several minutes and decreases with an increase in the temperature. It was found by ESR spectroscopy that these radical species decompose with cleavage of the Pt—Sn and Pt—Ge bonds, elimination of MCl_2, and the formation of radical **1a** (Schemes 5 and 6). The rate constants for the unimolecular decomposition of **4b** are 2.27, 6.24, and $8.4 \cdot 10^3$ s^{-1} at 323, 348, and 353 K, respectively, and the enthalpy of elimination is 10.2 kcal mol^{-1}.

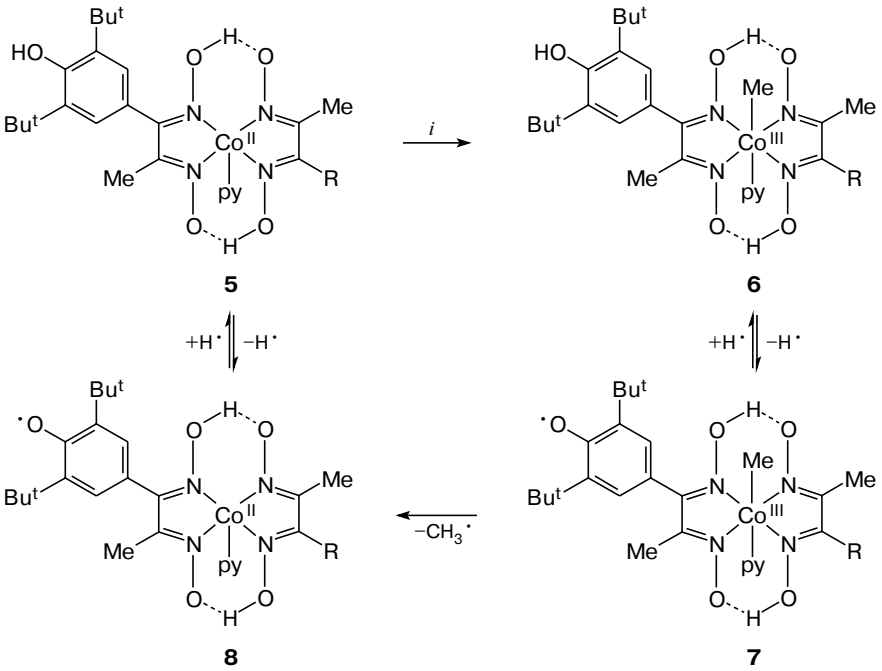
Scheme 6



This process can be explained by assuming that the organometallic group, $Pt(PPh_3)_2MCl_2$, undergoes intramolecular activation due to the oxidation of the organic ligand and the change in its magnetic state. This results in MCl_2 elimination in the rate-determining step and fast recombination of the Pt^I-containing coordinationally unsaturated species with the Cl atom in the solvent cage (elimination of MCl_2 from compounds **3a,b** cannot be detected even when the temperature is raised to 90 °C). It should be emphasized, however, that the whole cycle of formation, oxidation, and decomposition of compounds **3a,b** is reversible (see Scheme 5).

Similar reversible transformations subject to the long-range effect of the unpaired electron of the radical fragment of the ligand on the organometallic group are also observed for methylcobaloxime containing 2,6-di-*tert*-butylphenol[47] (Scheme 7). It was shown by ESR

Scheme 7



R is 3,5-di-*tert*-butyl-4-hydroxyphenyl

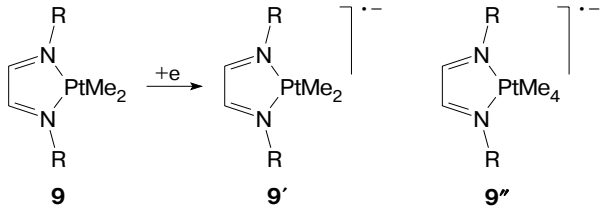
Reagents and conditions: *i*. 1) $NaBH_4$, NaOH, MeOH, −10 °C; 2) Me_2SO_4, 20 °C.

and electronic absorption spectroscopy and by kinetic measurements that, unlike the arbitrary decomposition of methylcobaloxime **6** in solutions, which proceeds over a period of 18 days (in methanol), dealkylation of the radical form **7** requires 5 h, indicating a promotory effect of the ligand unpaired electron on the Co—C bond cleavage. When the reaction medium contains methyl-group acceptors such as Hg, Cd, Sn, and Pb salts, the methyl group is transferred almost instantaneously to a metal atom by an alkylation mechanism.[59] This reaction occurs at a rate detectable on the ESR time scale. With excess metal salt, the reaction kinetics obey a first-order equation.

The possibility of transfer of a methyl group to a metal atom under conditions of electrochemical activation by homolysis of the Pt—C bond in paramagnetic organometallic compounds was detected[48] for compounds **9** by the ESR method. Single-electron reduction results in the generation of the corresponding radical anion **9′** (Scheme 8, see Table 1). The ESR spectrum exhibits also a well-resolved signal corresponding to radical anion **9″**.

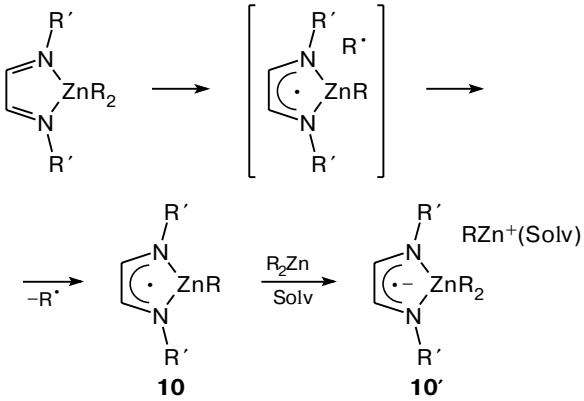
The researchers explained this unusual result (formal oxidation of the metal ion under conditions of reduction), obtained in the reduction of the initial diamagnetic Pt^{II} complexes in an electrochemical cell at 20 °C, by assuming that the methyl group is transferred to the coordinationally unsaturated Pt^{II} atom, apparently, in a bimolecular disproportionation reaction.

Scheme 8



R = Bu^t, 4-MeC_6H_4, *cyclo*-C_6H_{13}, 2,6-$Me_2C_6H_3$

Scheme 9



R = Me, Et, Pr^i, Ph; R′ = Bu^t, 2,6-$Me_2C_6H_3$;
Solv is a donor solvent

Table 1. Parameters of the ESR spectra of metal complexes (293 K)

Compound	Solvent	*g*-Factor	a_H(2 H)	a_Y[a]	a_M(1 M)	Ref.
				mT		
1a (X = Cl)	Toluene	2.0079	0.12	1.6 (a_P(2 ^{31}P))	9.4 (^{195}Pt)	45
1b (X = Cl)	Toluene	2.0051	0.15	1.87 (a_P(2 ^{31}P))	0.55 (^{105}Pd)	45
4a	Benzene	2.01	0.13	1.9 (a_P(2 ^{31}P)) 1.6 ($^{117/119}$Sn)	7.75 (^{195}Pt)	46
4b	Benzene	2.01	0.15	1.75 (a_P(2 ^{31}P))	7.33 (^{195}Pt)	46
8[b]	Toluene	2.0049	[c]	0.43 (a_N(2 ^{14}N))	0.43 (^{59}Co)	47
9′ (R = *cyclo*-C_6H_{13})	MeCN	2.090 (g_1), 2.016 (g_2), 1.944 (g_3)	—	—	6.5 (^{195}Pt)	48
9″ (R = *cyclo*-C_6H_{13})	MeCN	2.003 (g_1), 2.003 (g_2), 1.997 (g_3)	—	—	7.5 (^{195}Pt)	49
10 (R = Bu^t, R′ = Me)	Hexane	—	—	0.49 (a_N(^{14}N)), 0.59 (a_N(^{1}H))	0.05 (ZnMe)	49
10′ (R = Bu^t, R′ = Me)	THF	—	—	0.55 (a_N(^{14}N)), 0.55 (a_N(^{1}H))	0.298 (6 ^{13}C)	49
12	Toluene	2.004	0.1	0.2 (a_N(2 ^{14}N))	—	50
13a	CH_2Cl_2	2.0052	0.21	0.21 (a_N(1 ^{14}N))	0.2 (^{105}Pd)	51
13b	CH_2Cl_2	2.0083	0.1	0.28 (a_N(1 ^{14}N))	28.4 (^{195}Pt)	51
13c	THF	2.0053	0.1	0.28 (a_N(1 ^{14}N))	0.12 (^{105}Pd)	51
14	THF	2.0044	0.2	0.16 (a_N(2 ^{14}N))	0.32 (^{199}Hg)	52
16a	Toluene	2.0051	0.18	0.09 (a_H(4 H))	0.54 (^{105}Pd)	40, 41
17d (M = Zn)	CH_2Cl_2	2.005	0.2	—	—	53
18a (M = Zn)	Toluene	2.0043	0.2	—	—	54
19	Toluene	2.0046	0.13	0.3 (a_H(1 H)), 0.3 (a_N(^{14}N)), 0.13 (a_H(2 H))	—	55
20	Toluene	2.005	0.22	—	—	56
27[d]	Py	2.182 ($g_\perp$), 2.016 ($g_\parallel$)	—	5.97 ($A_\perp$), 7.36 ($A_\parallel$)	1.11 ($a_{N,\perp}$(^{14}N)), 1.62 ($a_{N,\parallel}$(^{14}N))	57
28	DMF	2.0045	0.2	—	—	58
29	DMF	2.0049	—	[e]	—	57
30	Toluene—DMF (5%)	1.985 ($g_\perp$)[f], 1.973 ($g_\parallel$)	—	—	—	57
	Toluene—Py (5%)	1.983 ($g_\perp$)[f], 1.97 ($g_\parallel$)	—	—	—	

[a] HFC with the magnetic nuclei of the coordinating group of the ligand.
[b] The ESR spectrum of compound **7** is similar in parameters to that of compound **8** but exhibits additional splitting of each line due to the HFC with the Me group at the Co atom.
[c] The HFC is not manifested because a_H(2 H) lies within the line width.
[d] $R_4PcCo^{II}Py_2$.
[e] The multiplet is poorly resolved.
[f] T = 77 K.

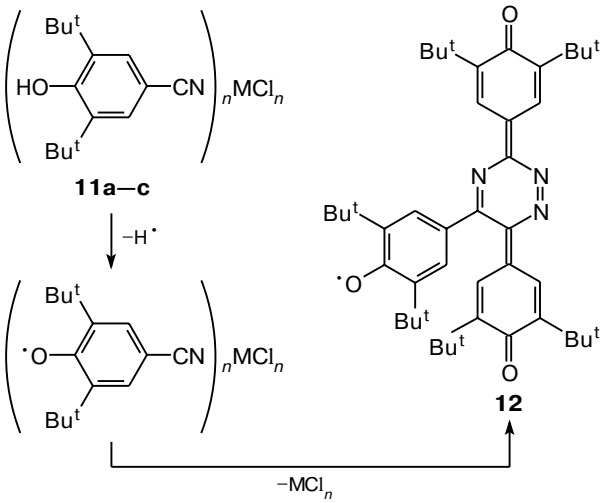
The thermally and photochemically induced transfer of alkyl groups to various organic substrates, induced by dissociation of the metal—carbon bond in paramagnetic organozinc compounds, has been studied using a set of physicochemical methods[49] (Scheme 9, see Table 1).

An unusual example of intramolecular transformation of the oxidized (radical) form of a ligand in the coordination sphere of a metal was found[50] for Pd^{II}, Pt^{II}, and Rh^{III} nitrile complexes (Scheme 10).

Ligand oxidation in complexes **11a—c** (see Scheme 10) yields a stable phenoxyl radical in which, according to ESR data, a substantial part of the spin density is located on the N atom, which results in changed MO of the complexes, distorted geometry, and destabilized metal—ligand bond[60] (see the contributing structures in Scheme 11).

This is followed by cyclotrimerization giving rise to stable paramagnetic nonsymmetrical triazine **12**, which was isolated in the solid state. Catalytic cyclotrimerization of benzonitrile into *symm*-triazine in the presence of transition metal salts has been described previously.[61] It is also known that nitriles activated by the coordination to Pd^{II} or Pt^{II} atoms are attacked by nucleophiles at the

Scheme 10

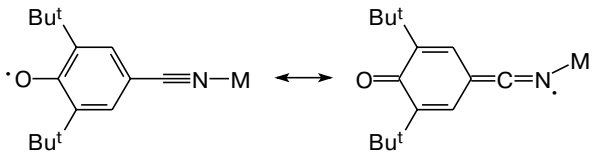


11a—c

12

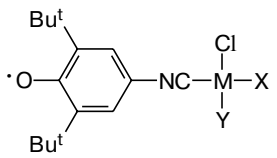
11a: M = Pd, n = 2; **11b:** M = Pt, n = 2; **11c:** M = Rh, n = 3

Scheme 11



nitrile C atom, giving rise to various five- and six-membered heterocycles in which the N—M bond is, nevertheless, retained.[62] In the absence of metal salts, this reaction does not proceed. In the case of the diamagnetic phenolic form of substituted benzonitrile, this reaction does not occur even in the presence of MCl_n. Data of ESR spectroscopy and analysis of the reaction products formed in the catalytic cyclotrimerization of a paramagnetic ligand suggest the following sequence of steps: activation of the complex upon oxidation and transfer of the ligand in the paramagnetic state; molecular transformation of the ligand in the metal coordination sphere; and the formation of the final paramagnetic product containing no metal ion.

Conversely, Pd^{II} and Pt^{II} complexes with 2,6-di-*tert*-butyl-4-isocyanophenol are converted upon oxidation into fairly stable paramagnetic species **13a—c**,[51] whose ESR spectra display coupling of the unpaired electron spin with the ^{195}Pt or ^{105}Pd nucleus (see Table 1).

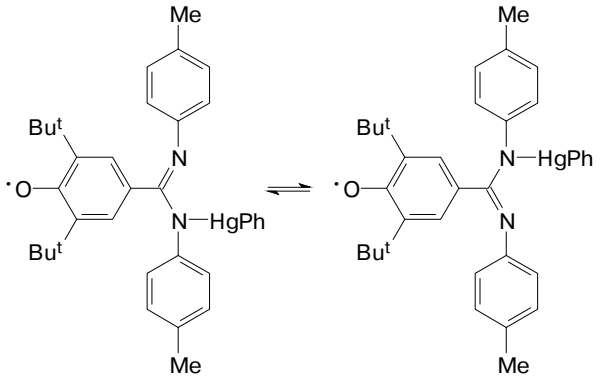


13a—c

13a: M = Pd, X = Cl, Y = PPh_3; **13b:** M = Pt, X = Cl, Y = PPh_3; **13c:** M = Pd, XY — η^3-All

A change in the type of metal—ligand bonding and in the geometry of complexes without their destruction was demonstrated[52] in an ESR study of Hg^{II} amidine complexes (Scheme 12).

Scheme 12

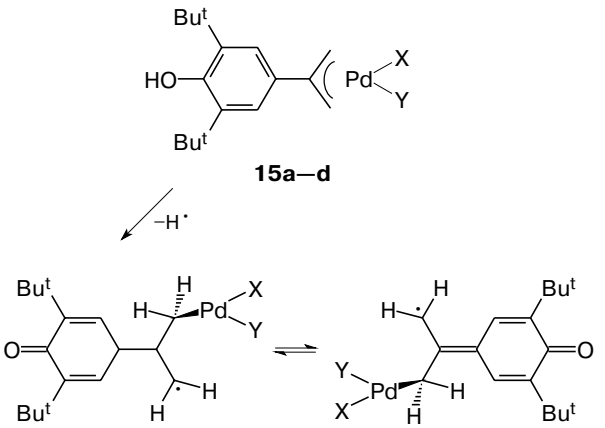


14

The tendency of the Hg^{II} atom to form linear structures is manifested as fast 1,3-migration of the phenylmercurio group in radical **14** (see Table 1).

The decrease in the activation barrier to the intramolecular π—σ-rearrangement (change in the type of the metal—ligand bond) as a result of ligand oxidation has been studied in detail[40,41] for a series of π-allyl Pd^{II} complexes (**15**, **16**) (Scheme 13).

Scheme 13



15a—d

16a—d

a: X = Y = μ-Cl; **b:** X = Cl, Y = PPh_3; **c:** XY = acac; **d:** XY = η^5-Cp

Unlike diamagnetic compounds **15a—d**, which undergo the π—σ-rearrangement, known in the chemistry of π-allyl complexes,[63] only when the temperature has been raised to 80—100 °C or after addition of a strong donor ligand, the change in the type of the π-allyl (η^3)—Pd and σ-allyl (η^1)—Pd bonds takes place at 20 °C

during transition of the ligand in the radical state (**16a—d**). This is manifested in the spectra as equivalence of the protons of the terminal methylene groups having equal HFC constants (see Table 1). In diamagnetic compounds, the *syn*- and *anti*-protons of the allylic fragment are magnetically nonequivalent, according to NMR data; for example, those in compound **15a** are recorded at 4.1 (2 H_{syn}) and 2.88 ppm (2 H_{anti}) in $CDCl_3$. The ESR spectral pattern does not change in the temperature range of −60 to 20 °C; only a slight increase in the a_{Pd} value is observed (for **16a**, a_{Pd} is 1.31 and 1.37 mT at 20 and −60 °C, respectively). This result is consistent with the view that the rate of the sigmatropic rearrangement decreases at low temperatures. The predominant contribution of the σ-structure (at 20 °C) results inevitably in a decrease in the overall degree of delocalization of the unpaired electron through the methylene group and influences the a_M values.[64] Intramolecular transformations are also observed for Pd^{II} diene complexes upon photochemical activation, which induces ligand oxidation to a radical cation.[65] On exposure to UV radiation with λ = 366 nm in acetonitrile, isomerization of 1,5-cyclooctadiene into 1,3-cyclooctadiene takes place; the driving force of this process is the charge transfer from the π-bonding MO of the ligand to the metal, which yields the intermediate radical cation form of the ligand (Scheme 14).

Scheme 14

$$(1,5\text{-COD})PdCl_2 \xrightarrow{h\nu} COD^{\bullet+}Pd^{I}Cl_2^-$$

COD is cyclooctadiene

This reaction carried out in a coordinating solvent (MeCN) involves elimination of the 1,3-isomer of the ligand and results in the synthesis of a palladium acetonitrile complex (Scheme 15).

Scheme 15

$$(1,5\text{-COD})PdCl_2 + 2\ MeCN \xrightarrow{h\nu} Pd(MeCN)_2Cl_2 + 1,3\text{-COD}$$

When ethanol is used as the solvent, the reaction is accompanied by the reduction of Pd^{II} to Pd^0 and gives the free ligand as the 1,3-isomer. Similar ligand transformations are also typical of Co^{III} complexes with amines under photoinitiation conditions.[66]

Thus, most organometallic and coordination compounds based on 2,6-di-*tert*-butylphenol tend to undergo intramolecular transformations upon the change in the magnetic state of the ligand. These processes can be responsible for the change in the complex geometry and the type of the metal—ligand bond and, in some cases, they result in bond cleavage. In general, the coordinated group (L) in structure **D** is not a kinetically independent redox center but serves as a conductor (mediator) of electronic interactions.

Porphyrins and phthalocyanines containing 2,6-di-*tert*-butylphenol fragments in the ligands

Metalloporphyrins (MP) and their analogs, metallophthalocyanines (MPc) are unique multielectron redox systems.[4,24—33] Development of the chemistry of these macrocyclic compounds has provided the basis for the design of materials whose properties are dictated by reversible transfer of one or several electrons.[67] The energy characteristics of ligand MO ($a_{1u}(\pi)$, $a_{2u}(\pi)$ are HOMO and $e_g(\pi^*)$, $b_{1u}(\pi^*)$ are LUMO) and the MO of metal atoms ($d_{z^2}(a_{1g})$, $d(e_g)$) ensure the possibility of stepwise two-electron oxidation and four-electron reduction of the macrocyclic ligand, the change in the oxidation state of the transition metal, and the existence of several low-energy metal—ligand (MLCT) and ligand—metal (LMCT) charge transfer bands, which are observed by spectroscopy in the visible and near-IR regions.

The introduction of the 2,6-di-*tert*-butylphenol fragments as substituents in the macrocycles of porphyrin or phthalocyanine free bases (the data of semiempirical PM3 and AM1 calculations) virtually does not change the energies of the frontier MO[68,69] and does not induce (according to X-ray diffraction data[70]) structural changes in the molecules of their complexes.

The metalloporphyrin and phthalocyanine molecules have two redox-active centers: the metal atom and the macrocyclic ligand; hence, in the simplest cases of single-electron reduction and oxidation, these systems can be classified as types **B** and **C**. For these systems, as in the above-considered cases, IET in the ligand—metal pair takes place.

For example, an interesting process was found for cobalt tetra-*tert*-butylphthalocyanine, namely, intramolecular transfer of an electron upon mechanical treatment of a solid sample[71] (Scheme 16).

Scheme 16

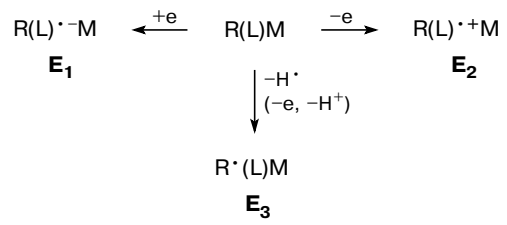
$$(Bu^t_4Pc)^{\bullet+}Co^{II} \rightleftharpoons Bu^t_4PcCo^{III}$$

Pc is phthalocyaninato dianion

The generation of the phenoxyl radical in the ligand macrocycle of porphyrin and phthalocyanine transition metal complexes opens up the way for developing systems with three redox-active centers (R, L, and M) (Scheme 17).

Thus, the rearrangement of the electronic system of the molecule can occur either with competitive participation of redox-active L—M, R—L, and R—M pairs or as a result of parallel or consecutive redox transitions involving several centers. Both kinetic (the rates of

Scheme 17

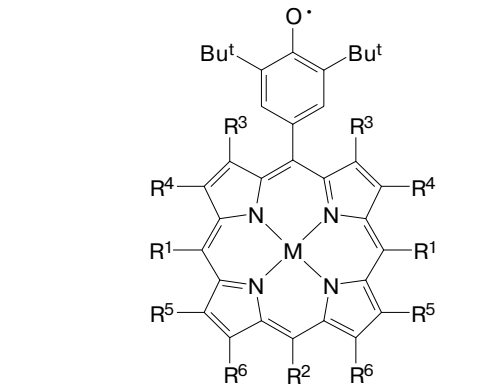


R is 3,5-di-*tert*-butyl-4-hydroxyphenyl; R• is 3,5-di-*tert*-butyl-4-hydroxyphenoxyl radical; L is porphyrinato or phthalocyaninato dianions

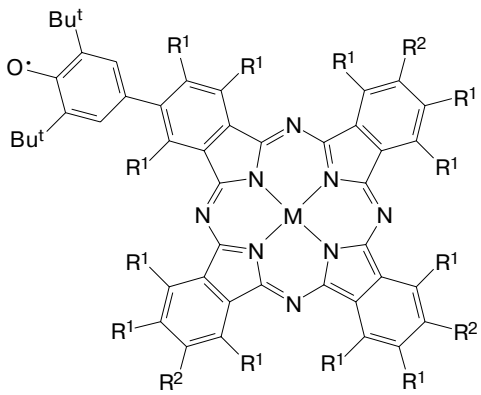
particular steps) and thermodynamic (the stability of particular species) factors are crucial in these processes.

The main requirement to the models of this type is the presence of either a C—C σ-bond linking the phenolic residue to the macrocycle or a conductive group between the phenolic fragment and the macrocycle, which provides the common conjugation system. In the absence of any linking group, the planes of the phenolic aromatic ring and the macrocyclic ligand are not coplanar. According to X-ray diffraction data, the dihedral angles between them are 66.9° and 67.6° for *mezo*-R_4PZn and *mezo*-R_4PPd (R is 3,5-di-*tert*-butyl-4-hydroxyphenyl), respectively.[70] In the formation of the phenoxyl radical, the contribution of the resonance quinoid structure accounts for the partial double bonding between the phenoxyl and macrocycle carbon atoms and thus ensures the larger extent of interaction between the π-systems. The ESR spectra of the phenoxyl radicals attached to a porphyrin or phthalocyanine ring are triplets, indicating couping between the unpaired electron spin and the *meta*-protons of the phenoxyl ring (**17a—d**, **18**);[40,41,53—56,58,72—76] a_H(2 H) is 0.16—2 mT (see Table 1).

The HFC constants with other nuclei manifest themselves when the phenoxyl radical and the macrocycle are linked by various groups, for example, the —CH=N group (**19**)[55] but not by the —CONH group (**20**)[56] (see Table 1).



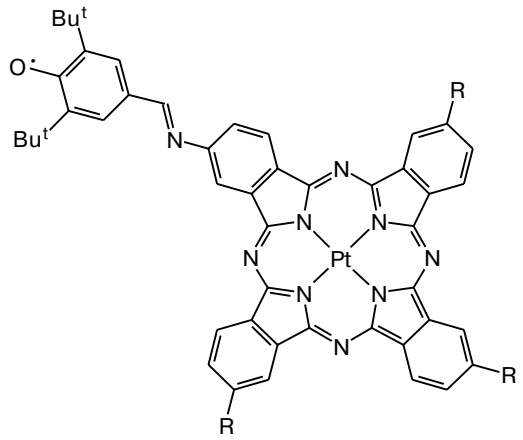
17a—d



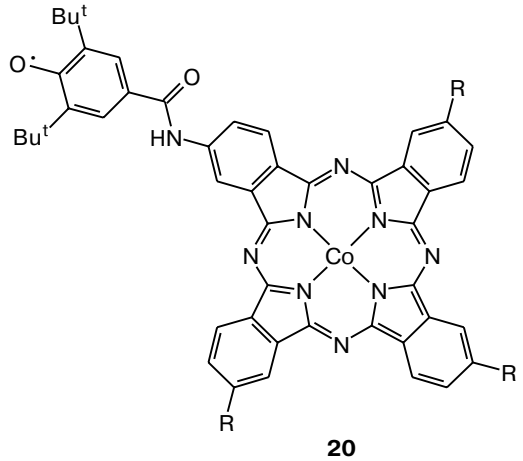
18

17a: R^1—R^4 = H, R^5 = R^6 = Me; M = HH, Zn, Fe
17b: R^1 = R^2 = H, R^3 = R^6 = Me; M = HH, Zn, Fe
17c: R^1 = H, R^2 — 3,5-di-*tert*-butyl-4-hydroxyphenyl; R^3 = R^6 = Me, R^4 = R^5 = Bu; M = HH, Zn, Fe
17d: R^1 = R^2 = 3,5-di-*tert*-butyl-4-hydroxyphenyl, R^3—R^6 = H; M = HH, TiO, VO, MnCl, Fe, Co, Ni, Cu, Zn, GaCl, Pd, $SnCl_2$, Pt
18: R^1 = Cl, R^2 = 3,5-di-*tert*-butyl-4-hydroxyphenyl; M = HH, Mg, Fe, Co, Ni, Cu, Zn, Pd, Pt, NdPc, EuPc, LuPc

Pc — phthalocyaninato dianion



19



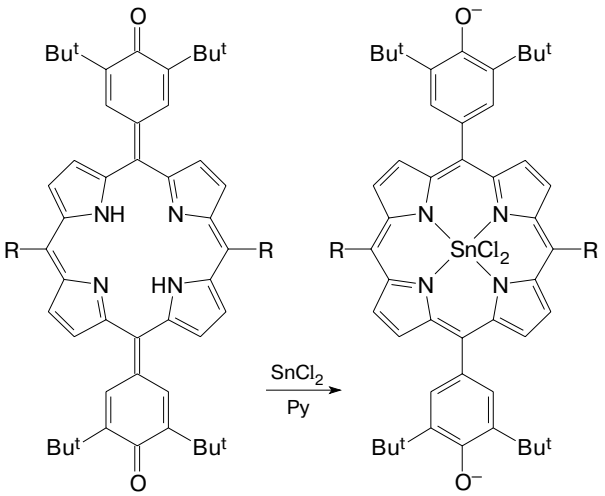
20

19: R is *N*-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)imino group

20: R is *N*-(3,5-di-*tert*-butyl-4-hydroxybenzoyl)amino group

The data of quantum-chemical calculations (PM3, AM1), electronic absorption spectroscopy, and electrochemistry and the composition of the reaction products[40,53,57,58,72,77–80] show the change in the reactivity of compounds of this type upon ligand oxidation; in some cases, the fact of IET was established. For example, the attempt to introduce the Sn^{II} ion into the free base of the product of two-electron oxidation of tetrasubstituted porphyrin **21** entails intramolecular oxidation of Sn^{II} to Sn^{IV} and reduction of two quinoid substituents (Scheme 18).

Scheme 18

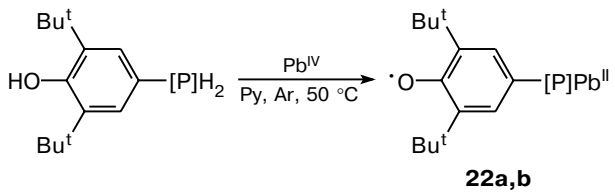


21

R is 3,5-di-*tert*-butyl-4-hydroxyphenyl

Upon the oxidation of free bases of phenol-containing porphyrins (sources of radicals **17a,b**) by Pb^{IV} compounds, the spectrum shows the presence of Pb^{II} porphyrins containing the ligand with an open electron shell as a neutral (noncharged) radical[40] (Scheme 19).

Scheme 19



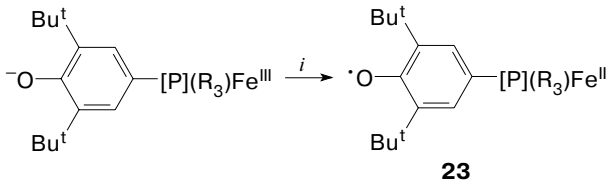
22a,b

22a: [P] is 12,13,17,18-tetramethylporphyrinato dianion
22b: [P] is 2,3,7,8,12,13,17,18-octamethylporphyrinato dianion

The ESR spectra of the oxidation products correspond to phenoxyl radicals **22a**,**b** (g ~2.004, a_H(2 H) = 0.18 mT). It is known[81] that, according to electronic absorption spectra, Pb^{II} porphyrins are p-type hyperporphyrins. The spectra exhibit additional bands for the allowed $a_{2u}(6p_z Pb^{II}) \rightarrow e_g(\pi^*)$ transitions in the region of 450 nm, which is consistent with the obtained data and confirms the change in the metal oxidation state. Metal porphyrins with this type of spectral characteristics are used as models of cytochrome P_{450}.

Iron(III) porphyrins with 2,6-di-*tert*-butylphenol fragments, which correspond to d-type hyperporphyrins according to their spectral characteristics, were also used as model compounds to study the redox properties of cytochrome P_{450}.[72,82,83] In the presence of *N*-methylimidazole, which occupies two axial positions, intramolecular reduction of Fe^{III} to Fe^{II} takes place, the phenol group acting as the reducing agent in the form of phenoxide ion (Scheme 20).

Scheme 20



23

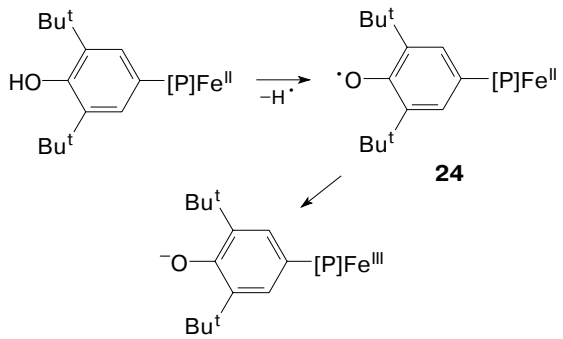
R is 3,5-di-*tert*-butyl-4-hydroxyphenyl;
[P] is 12,13,17,18-tetramethylporphyrinato dianion

Reagents: *i*. *N*-methylimidazole.

It is noteworthy that this process also occurs upon the addition of CO to the reaction medium; in this case, the formation of the ternary *N*-methylimidazole—porphyrin—CO complex was detected,[82] which makes it possible to model intra- and intermolecular electron transfer, observed in the active centers of heme-containing enzymes.

In the case of oxidation of the phenolic group in Fe^{II} porphyrin, back transfer of an electron from Fe^{II} to the ligand takes place, resulting in the reduction of the phenoxyl radical to the phenoxide ion[40] (Scheme 21).

Scheme 21



24

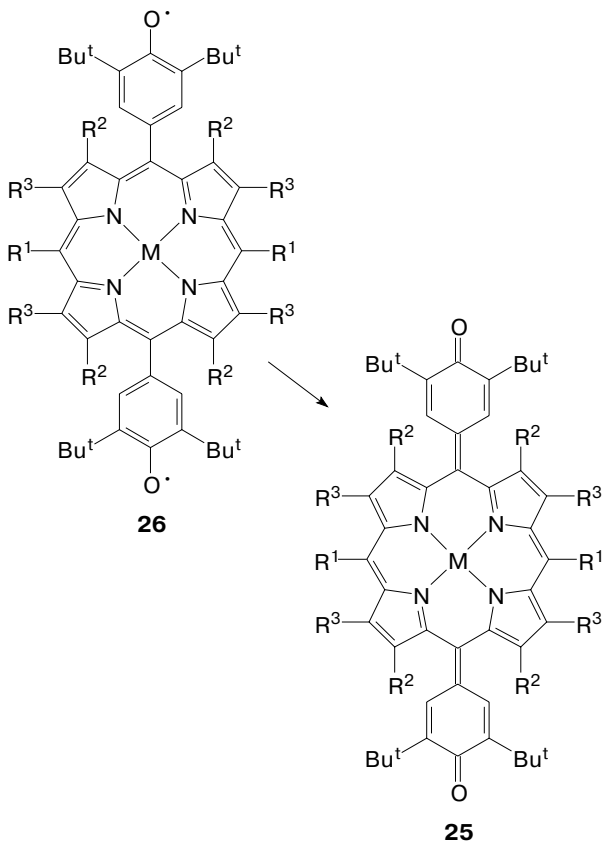
[P] is 2,3,7,8,12,13,17,18-octamethylporphyrinato dianion

Intramolecular processes are detected by ESR and electronic absorption spectroscopy; this confirms the

generation of radicals with localization of the unpaired electron in the ligand and of d-type iron hyperporphyrins with allowed transitions from the ligand $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals to the metal $e_g(d_\pi)$ orbital, exhibited in the absorption spectra in the region of ~370 and 450 nm, respectively.

When the porphyrin molecules contain a redox-active phenolic fragment, the activation barriers to the IET decrease; this results in exchange electronic processes involving the ligand HOMO (a_{2u}) and the metal $b_{2g}(d_{xy})$ or $e_g(d_\pi)$ orbital, close in energy. The thermodynamic stability of the resulting redox forms of porphyrins is fairly high. Their steady-state concentration in solutions under an inert atmosphere allows detection of these species by physicochemical methods and detection of the electronic transitions in the R and M pair of redox-active centers. However, the ease of transformation of the aromatic porphyrin macroligand into porphodimethene accounts for the formation of diamagnetic products with quinoid groups (**25**) in the case of di- and tetrasubstituted porphins, when they undergo reversible two-electron oxidation with the intermediate formation of unstable biradicals **26** [40,72,82,83] (Scheme 22).

Scheme 22



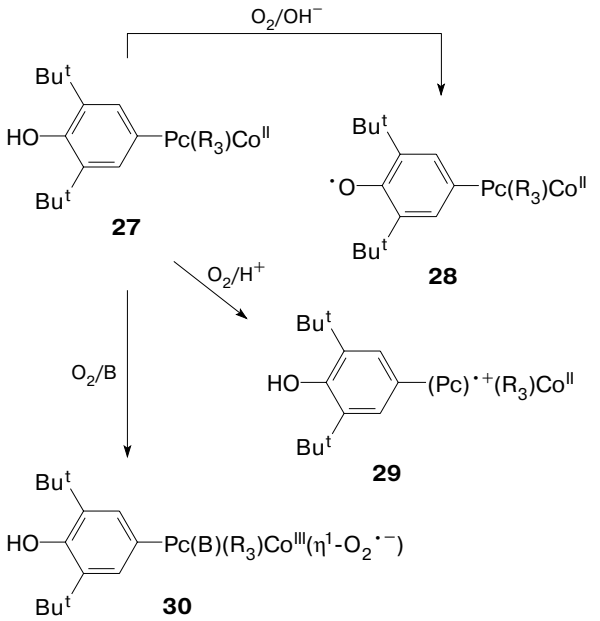
26 **25**

R^1 = H, 3,5-di-*tert*-butyl-4-hydroxyphenyl; R^2 = H, Me; R^3 = H, Bu; M = HH, MnCl, FeCl, Co, Ni, Cu, Zn, Pd, Pt

Molecular oxygen can also function as the oxidant (in the basic medium), which hampers investigation of the redox properties of these compounds in air. The high stability of metallophthalocyanines in the ground state and of virtually all their redox forms[33] provides the possibility of studying the properties of these compounds even under aerobic conditions at room temperature.

The behavior of metal complexes under conditions of redox reactions in the presence of molecular oxygen is a very important point, because this determines the possibility of using these compounds as catalysts and various materials in air. It was shown for Co^{II} phthalocyanine with phenol fragments in the macrocycle[57,58,80] that the reaction pathway depends on the medium acidity so crucially that O_2 can act as the oxidant with respect to either the phenol fragment, or the phthalocyanine macrocycle, or the metal ion (Scheme 23).

Scheme 23



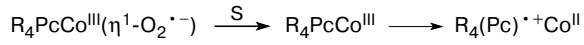
27 **28** **29** **30**

B is base (Py, DMF); R is 3,5-di-*tert*-butyl-4-hydroxyphenyl; Pc is dodecachlorophthalocyaninato dianion

The differences between the electronic absorption spectra and the ESR spectra of species **27—30** (see Table 1) allow unambiguous identification of the products of redox reactions.

Intramolecular transformations in the phthalocyanine ligand—metal pair (L—M) readily occur in superoxo complex **30** when a substrate capable of being oxidized by O_2, for example *o*-aminophenol, is added to the reaction medium.[84] In the process studied, complex **27** is a catalyst; its transformations are detected not only by physicochemical methods but also by analysis of the final reaction products (Scheme 24).

Scheme 24

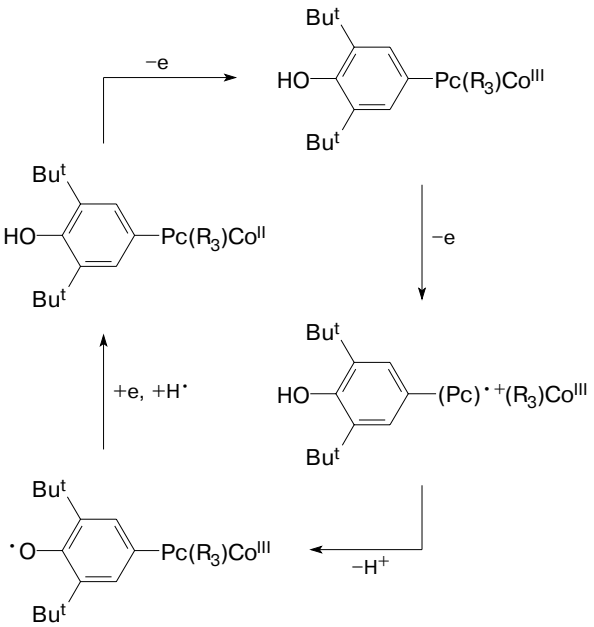


R is 3,5-di-*tert*-butyl-4-hydroxyphenyl;
Pc is dodecachlorophthalocyaninato dianion; S is *o*-aminophenol

This process is facilitated by the possibility of the removal of the axial ligand, superoxide ion, by the substrate, which is coordinated to the second axial position to form a complex of the substrate—catalyst—oxygen type (which is confirmed by the Michaelis—Menten kinetic equation) and is oxidized to 2-aminophenoxazin-3-one.

The electron transfer in the phthalocyanine ligand—phenolic group pair (R—L) takes place under more rigorous conditions in the presence of a strong oxidant (Br_2) and is observed as the step next to the oxidation of the metal ion[58] (Scheme 25).

Scheme 25

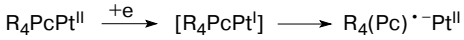


R is 3,5-di-*tert*-butyl-4-hydroxyphenyl;
Pc is dodecachlorophthalocyaninato dianion

All the intermediates involved in the cycle (see Scheme 25) exhibit characteristic absorption and ESR spectra, pointing to localization of the unpaired electron in particular redox-active sites (R, L, or M). The main requirement to the type **E** systems, *i.e.*, reversibility of the redox transformations without destruction of the complex, is fulfilled in this case.

The first (single-electron) step of reduction of phthalocyanines of this series cannot involve the phenolic fragment; the additional electron occupies the $e_g(\pi^*)$ LUMO of the ligand or (in most cases), the metal d_{z^2} orbital. However, in some cases, for example, for the Pt^{II} complex, the experimental data obtained by different methods, namely, electronic absorption spectroscopy, cyclic voltammetry, and ESR spectroscopy are at variance with each other.[77,85] Thus the absorption spectrum recorded for the reduction of R_4PcPt^{II} exhibits absorption maxima for the $e_g(\pi^*) \rightarrow b_{1u}(\pi^*)$ electronic transitions corresponding to the radical anion derived from the macrocycle, while the ESR spectrum (77 K) contains a signal with a *g*-factor of 1.9839 corresponding to the Pt^{I} complex (the *g*-factor for the ligand radical anion is 2.0014). The preferred reduction of the metal also follows from the data on the dependence of the half-wave reduction potential ($E_{1/2}^{red}$) on the second ionization potential of the metal IP_2. This seeming contradiction is explained by the possibility of IET: the Pt^{I} complex is kinetically unstable and is rapidly converted into the stable Pt^{II} complex with the ligand reduced to the radical anion[85] (Scheme 26).

Scheme 26



R is 3,5-di-*tert*-butyl-4-hydroxyphenyl;
Pc is dodecachlorophthalocyaninato dianion

Thus, it becomes evident that the intramolecular exchange electronic interactions observed in macrocyclic metal complexes with phenolic substituents include complete electron transfer in pairs (R—L, L—M, R—M) or the change in the electronic structure (and, hence, reactivity) due to the appearance of an unpaired electron in the substituent. The direction and the character of intramolecular processes depend on essential factors (molecular structure, thermodynamic and kinetic stability of the redox forms, the possibility of introduction or elimination of axial ligands, *etc.*) and on external factors (nature of the redox reagent, medium, temperature). The investigation method is also important: the mechanisms should be interpreted only based on a set of various physicochemical methods. It should be emphasized that in this case, the macrocyclic ligand L not only acts as the conductive conjugated bridge between the redox centers (R group and M atom) and fixes the complex geometry but can also function as a kinetically independent redox site of the system.

* * *

The results of studies of organometallic and coordination compounds with redox-active 2,6-di-*tert*-butylphenol fragments in the ligand lead to the conclusion that the change in the magnetic state of the ligand (transfer into paramagnetic form) ensures the possibility of directed activation of metal complexes. It can be assumed that the 2,6-di-*tert*-butylphenol residue is not a unique redox group. Type **D** systems (R•LM) can, in

principle, contain other fragments, the main requirement to them being the existence of easy and reversible transitions proceeding by either an outer- or an inner-sphere mechanism:

$$(R^-)LM \overset{+e}{\rightleftharpoons} (R^\bullet)LM \overset{-e}{\rightleftharpoons} (R^+)LM.$$

Studies of multielectron redox systems of this type based on various metal complexes are mainly aimed at solving the following problems: (1) determination of the rates and activation energies of IET; (2) elucidation of the fine mechanism of IET (what is the optimal distance for IET and what mechanism, either through-space or through the system of bonds, does it follow); (3) identification of conditions under which the process is adiabatic or nonadiabatic. From the viewpoint of synthetic problems, it is of interest to prepare cage structures with several metal atoms and redox-active groups in the ligands. Generally, the progress along this line of research can ensure the possibility of designing multielectron metal complex redox systems responding to mild peripheral impact on the organic part of the molecule.

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