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The Unpaired Electron in Transition Metal Complexes

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The present state of research into complex and organometallic compounds with an unpaired electron is described. Paramagnetic complexes of transition metals, differing in the position of the free-radical fragment and in the nature of the paramagnetic ligands are examined. The possibility of investigating the intramolecular electron transfer in the metal-ligand system and the formation of intermediate free-radical products in reactions of transition metal compounds is discussed.
The bibliography includes 201 references.

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I. INTRODUCTION

The study of transition metal complexes carrying an unpaired electron presupposes two interrelated aspects. Firstly, the study of the possibility of intramolecular electron transfer in the metal–ligand system. Secondly, the elucidation of the question of what changes are undergone by the free radical while it is coordinated in the sphere of the metal. The first aspect is of interest in connection with the fact that there should exist an analogy between macromolecular biological systems responsible for electron transport and artificial models in which such transport is possible. The transition metal, capable of existing in various oxidation states, may play a decisive role in electron transport. On the other hand, the coordination of a free radical leads to a change in its fundamental characteristic, namely its reactivity. Furthermore, the free radical undoubtedly influences the electronic structure of the molecule of the complex.

The solution of the above problems has become possible as a result of the development of spectroscopic methods for the investigation of paramagnetic organometallic compounds. These compounds can be divided into three main types:

(1) Paramagnetic compounds whose properties are determined by the paramagnetism of the central metal ion, i.e. the so-called spin-unpaired complexes.

(2) Charged paramagnetic systems—radical-anions and radical-cations generated by one-electron reduction or oxidation and neutral radicals formed on photolysis, radiolysis, or chemical bond dissociation.

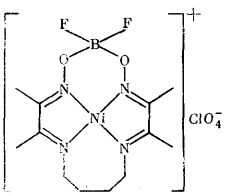
(3) Complexes with paramagnetic ligands.

Like any classification, such subdivision is to some extent arbitrary. Strictly speaking there exist two clearly distinguished limiting cases—transition metal complexes with an odd number of electrons in the *d* level and complexes with an unpaired electron located on the periphery of the ligand and virtually incapable of hyperfine interaction with the metal nucleus. Intermediate compounds are of greatest interest. In systems where there is a possibility of the delocalisation of an electron over the entire molecule, one may expect the occurrence of intramolecular electron transfer, which determines the functional similarity of such compounds with oxidation-reduction coenzymes.

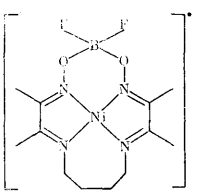
An example of intramolecular electron transfer is provided by the process occurring in the cofactor NAD (nicotinamide-adenine dinucleotide). The reduction of the cation NAD^+ leads to NAD·. Kinetic data have shown[1] that in the initial stages an electron adds to adenine and is then rapidly transferred to the nicotinamide component of the molecule, a signal due to the nicotinamide radical appearing in the EPR spectra. This mechanism has been proposed by analogy[2] for biological systems containing a transition metal ion. Intramolecular electron transfer has been postulated for cytochrome *c*, the one-electron oxidation of which results in the formation of the ferrocytochrome *c* radical-cation (the unpaired electron is localised in the porphyrin ligand). There is then rapid electron transfer within the molecule with participation of the iron atom and ferrihaemoprotein is formed[2]:

$$Fe^{II}Cyt\text{-}c \xrightarrow{-e} [Fe^{II}Cyt\text{-}c]^{\ddagger} \rightarrow Fe^{III}Cyt\text{-}c \ .$$

An interesting case of intramolecular electron transfer *in vitro* has been noted recently[3]; the nickel(II) complex



was obtained, its reduction by a one-electron reductant (cobaltocene) yielding a one-electron reduction product:



Two signals were observed in the EPR spectrum of this product in the frozen liquid-crystal phase: the first (g = 2.113) was assigned to a complex containing a paramagnetic nickel(I) ion and the second (g = 2.048) was

assigned to a radical-anion containing nickel(II). Thus there are two complexes in the first of which the unpaired electron is localised at the central nickel ion and in the second it is localised in the organic ligand. In other words the one-electron reduction of the nickel(II) complex with a macrocyclic ligand leads to the formation of two extreme forms of the reduced product, which are in equilibrium:

$$Ni^{II}(L^{\cdot-}) \underset{}{\overset{K=0.27}{\rightleftharpoons}} Ni^{I}(L) \ .$$

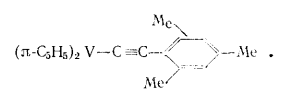
This example is an unusual instance of electronic tautomerism in solution and demonstrated the possibility of the artificial generation of metal-containing systems capable of effecting the intramolecular electron transfer. The search for and study of such systems may provide a key to the understanding of the most important catalytic and biochemical processes in which the transition metal and its chemical environment play a decisive role.

II. TRANSITION METAL COMPLEXES CONTAINING A PARAMAGNETIC CENTRAL ATOM

The first EPR data for paramagnetic transition metal complexes were obtained in 1957 [4,5] in studies of complex formation reactions. The method is applicable only to compounds containing a transition metal atom with an odd number of electrons in the *d* or *f* levels. The paramagnetism of the complexes is determined in this instance by the properties of the central ions with d^1, d^3, d^5, d^7, d^9, and f^7 configurations. Since numerous reviews and monographs have been devoted to studies of such complexes[6-14], they will not be considered in the present review. We should like to mention merely that the unpaired electron in such complexes may interact with the ligand environment. Fairly high constants for the hyperfine interaction (HFI) of the unpaired electron with the nuclei of the coordinating ^{14}N or ^{31}P atoms are characteristic of ligands containing heteroatoms (pyridine, isoquinoline, pyrazole, imidazole, triphenylphosphine, etc.).[15-17]

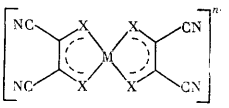
It has been shown[16] that the degree of delocalisation of spin density over the ligand depends on the geometry of the complex and increases on passing from an octahedral to a tetrahedral structure. The spin density can be delocalised via both π and σ metal–ligand bonds[18-21]. For π-complexes of the sandwich type, the interaction of the metal *d* orbitals with the π-electron system of the ligand leads to HFI with the ring protons; for example $a_H = 3.8$ G has been obtained for dinaphthalenevanadium(0).[22,23]

Cases of the formation of organic σ-complexes, in which a π-type transfer of spin density takes place, are also possible; for example, this happens in the following organometallic radical containing two unpaired electrons[24]:



The degree of delocalisation of the spin density to the acetylenic ligand is significantly greater than to the π-cyclopentadienyl ligands.

However, in many instances it is fairly difficult to establish the factor which determines the paramagnetism of the molecules of the complex. A change in the oxidation state of the metal in complexes, associated with the appearance of an odd number of electrons in the *d* level, can be achieved by the one-electron reduction (or oxidation) of the corresponding initial compounds. However, this entails the reduction (or oxidation) of the molecule as a whole and the change in the effective charge of the metal by unity is not an obligatory consequence of the process[25-33]. Thus the electrochemical reduction of the nickel-subgroup metal dithiolate complexes yielded the corresponding d^9 complexes:

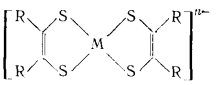


M = Ni, Pd, Pt; X = S, NH_2, $n = 1, 2$

It is believed[25] that the main process involves the one-electron reduction of the metal:

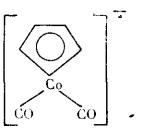
$$M^{II} \xrightarrow{-e} M^{I} \ .$$

The oxidation state of five, which is unusual for platinum and palladium, is attributed by the above investigators to the oxidised form of the dithiolene complexes of the quadrivalent metal formed in the reaction with bromine[26]:



M = Pd, Pt; R = CN, $n = 1, 2, 3$;
R = H, Alk, Ar, CF_3, $n = 0, 1, 2$.

The radical-anion of (π-cyclopentadienyl)cobalt(I)-dicarbonyl, formed as a result of γ-irradiation, has been called[30] a cobalt-centred radical:



A number of studies[31-33] have been made on the oxidised form of cobalt complexes with macrocyclic ligands, which are structural models of vitamin B_{12}. EPR data suggest that the central cobalt(II) ion is paramagnetic.

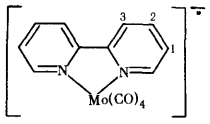
In the general case the possibility of the delocalisation of the spin density over the entire molecule is influenced by the nature of the metal–ligand bond[34-42].

The electronic "conductivity" of substrates depends not only on the nature of the metal but also on its ligand environment and is a characteristic property of enzyme-like molecules. The study of metal complexes with ligands capable of undergoing ready and reversible one-electron transitions, involving only partly the valence shell of the metal, is particularly promising in this connection.

III. CHARGED AND NEUTRAL PARAMAGNETIC COMPLEXES

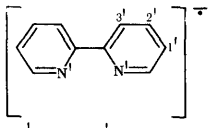
The first attempts to obtain and investigate organometallic radical-anions and radical-cations were made in the 1960's. At that time a series of communications by Dessy and coworkers[43-58] were published, describing the generation of charged paramagnetic species by the electrochemical oxidation (or reduction) of organometallic compounds. The study of the radical-anions of a series of chromium, molybdenum, tungsten, iron, and ruthenium complexes by various physicochemical methods enabled the authors of the above studies to reach conclusions, firstly, concerning the degree of delocalisation of the spin density by means of EPR studies, secondly, about the charge distribution (with the aid of the NMR method), thirdly, about the nature of the electric field gradient at the metal atom nucleus (with the aid of the Mössbauer method), and, fourthly, about the transmission of charged density via the metal atom (with the aid of infrared spectroscopy).

The constants for the hyperfine interaction of the unpaired electron with the ^1H and ^{14}N nuclei of bipyridyl coordinated in the bipyridylmolybdenum tetracarbonyl radical-anion and in the radical-anion of the free ligand have been compared[44]. The HFI constants (a, G) are smaller for aromatic protons in the radical-anion of the complex, while the constant for the HFI with the coordinating ^{14}N heteroatoms increases on passing from the free ligand to the complex. This permitted the conclusion that the organometallic group exhibits an electron-accepting effect in the redistribution of spin density.



$a_H^1 = 3.96$; $a_H^2 = 0.67$

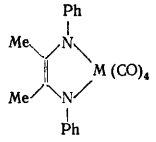
$a_H^3 = 1.2$; $a_N = 3.96$



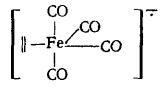
$a_H^{1'} = 4.96$; $a_H^{2'} = 0.7$

$a_H^{3'} = 1.4$; $a_N' = 2.48$

The change in charge density at the atoms of the organic ligand relative to the free ligand was estimated by NMR from the decrease in the chemical shift $\Delta\delta$ of the aromatic carbon atoms in the chromium, molybdenum, and tungsten complexes[57]:



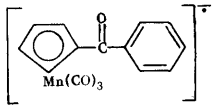
It was found that the charge is almost wholly localised at the metal atom. Mössbauer spectroscopic data confirmed the increase of electron density at the metal atom following the formation of a complex. It has been shown in relation to olefin complexes of iron that the spin density is mainly concentrated in the ligand:



Mössbauer spectra yield a lower σ-electron density on the nucleus of the iron atom, which is due to the increase of the s-electron shielding caused by the ligand → metal π-electron donation. Electronic absorption spectroscopic data have shown that the electron occupies the π^* orbital of the ligand, but most of the charge is "withdrawn" via the metal to the carbonyl groups[45].

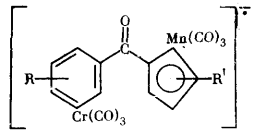
Thus the coordinated ligand in the L–M–CO system is an effective spin reservoir but a weak charge reservoir, i.e. the spin and charge are separated in the charged radical systems.

Chromium and manganese carbonyl complexes with ligands of the cyclopentadienyl and arene types have been investigated[59–61]. The benzoylcyclopentadienylmanganese tricarbonyl radical-anion has been obtained by reduction with metallic potassium:



Its EPR spectrum consists of six equal-intensity lines with $a_{^{55}Mn} = 7.68$ G. Each component of this sextet is split into a doublet (2.91 G) of triplets (1.03 G), which indicates the involvement of the ligand in the delocalisation of the spin density.

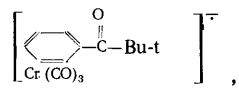
The electronic effects have been investigated for a series of substituted radical-anions obtained by the reduction of neutral complexes with metallic potassium in dimethoxyethane:



R = H, *o*-Me, *m*-Me, *p*-Me, *p*-OMe;
R' = H, α-Me, β-Me.

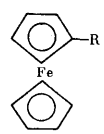
Signals due to the hyperfine interaction with the ^{55}Mn and ^{53}Cr nuclei and with the ligand protons have been observed in the EPR spectra of such radical-anions, $a_{^{55}Mn}$ depending on the positions of the substituents R and R'; the g-factor varies in the range 1.9989–2.0002; the constants $a_{^{55}Mn}$ range from 1.62 to 5.11 G; the constant a_{p-H} for the ligand protons is in the range 1.53–1.65 G, while a_{o-H} is in the range 0.78–2.70 G. Studies of the EPR spectra indicate an appreciable delocalisation of electron density over the entire chromium–benzoylcyclopentadienyl–manganese system, which can be accounted for solely by taking into account the appreciable π-overlap between the metal and ligand orbitals and also by the π-electron conjugation with the aromatic system.

Comparison with the benzoylcymantrene radical-anion described above makes it possible to elucidate the principal effect of the $Cr(CO)_3$ group—the delocalisation of the spin density over the entire system, including the $Mn(CO)_3$ group. The conclusions reached agree with the results of studies of the complexes by ^1H NMR and infrared spectroscopy[62–69]. In the arene complex of chromium with a t-butyl substituent at the carbonyl group[64],



it was not possible to observe the hyperfine interaction with the ^{53}Cr nucleus, as in the case of the carbonyl complexes $(CO)_5MC(R)Ph$, where M = Cr, Mo, or W and R = OMe or Ph.[65]

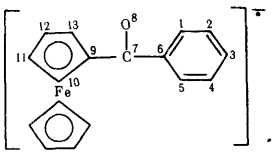
A large series of studies have been devoted to metallocenes, starting with the simplest representatives of compounds of this class—ferrocene[66] and its derivatives[67–72]:



R = Bz, CC_6H_4Me (O), NO_2, C_6H_4CN, CC_6H_4COOMe (O), $C_6H_4NO_2$.

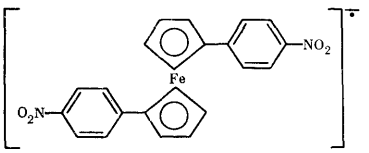
Comparison of the results of the calculation by the Hückel molecular orbital method with the observed hyperfine structure of EPR spectra[68] yields a quantitative distribution of the spin density in the radical-anion. Overall, the ferrocenyl group is destabilising compared with the phenyl group. In the presence of both groups in one molecule, the degree of delocalisation of the spin density is greater

in the direction of the benzene ring[69]:



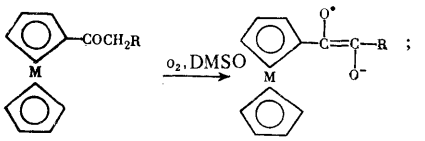
The following values have been obtained for the phenyl group: $a_H^1 = 3.3$ G; $a_H^5 = 2.91$ G; $a_H^2 = a_H^4 = 0.89$ G; $a_H^3 = 4.3$ G. In the ferrocenyl group the delocalisation involves only one cyclopentadienyl ring ($a_H^{10} = a_H^{13} = 0.89$ G).

In complexes with *p*-nitrophenyl substituents of the type

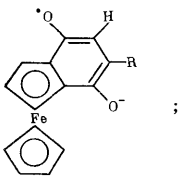


the unpaired electron is located almost wholly in the nitrophenyl fragment by virtue of the high electronegativity of the nitro-group ($a_N = 10$ G, which is close to the value for the nitrobenzene radical-anion), while the constants for the HFI with the protons of the cyclopentadienyl rings are small ($a_H \leq 0.3$ G).[67]

Stable paramagnetic semiquinones of the metallocene series are formed on oxidation of ketones containing the α-methylene group[70,71]:



M = Fe, Ru; R = Me, Et, iso-Pr, iso-Bu, Ph;
a_H(ring) = 0.57 G, a_H(Me) = 3.4-4.4 G.



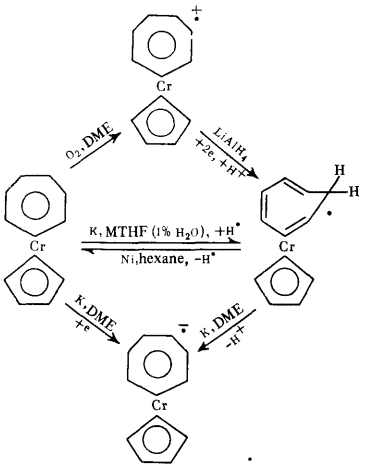
R = H, Me, Et, iso-Pr; a_H(ring) ≅ 0.4 G, a_H = 4.05 G, a_H(Me) = 3.47 G, a_H(Et) = 3.54 G, a_H(iso-Pr) = 3.35 G.

The ease of the one-electron oxidation of metallocene derivatives is confirmed by the formation of paramagnetic salts, where the anionic component may consist of the radical-anion derived from the organic one-electron acceptor tetracyanoquinodimethane (TCNQ):[73]

$$\{[Fe(C_5Me_5)_2]^+\}_2(TCNQ)_2^{2-}.$$

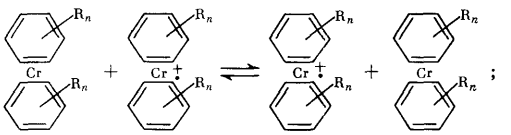
Such salts are in essence organometallic analogues of charge-transfer complexes.

An interesting cycle of one-electron transitions has been described for π-cycloheptatrienyl-π-cyclopentadienyl-chromium[74-76]†:



Lines due to the HFI of the unpaired electron with the ^{53}Cr nucleus have been observed in the EPR spectra of paramagnetic complexes of chromium ($a_{^{53}Cr} = 17.35$ G for the radical-anion, $a_{^{53}Cr} = 19.0$ G for the radical-cation, and $a_{^{53}Cr} = 19.7$ G for the radical). A change in $a_{^{53}Cr}$ is observed also for arene complexes of chromium[75].

The electron exchange in the arene π-complexes of chromium and their deuterated analogues has been investigated by EPR and ^1H NMR; the rate constants for the exchange have been measured and the influence on the latter by various substituents has been investigated[77,78]:



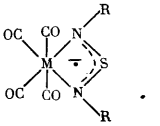
R_n = Me, 1,3-Me_2, 1,3,5-Me_3, 1,2,4,5-Me_4.

Paramagnetic complexes of chromium, molybdenum, and tungsten are formed also in the one-electron reduction of carbonyl complexes containing sulphur diimides as bidentate ligands[79]:

$$\{(CO)_4M[S(NR)_2]\}^{\bullet-};$$

R = t-Bu, Ph, 4-MeC_6H_4, 4-$O_2NC_6H_4$.

Analysis of the EPR spectra, calculations by the ENDO method, and comparison with the spectra of the radical-anions of the initial ligands $[S(NR_2)]^{\bullet}$ have led to the conclusion that the unpaired electron is localised in the ligand:



The radical-anions obtained are fairly stable; for example, the half-life of the chromium complex is 6 min.[79].

Cationic paramagnetic complexes of chromium containing carbenes as ligands can be obtained by one-electron oxidation. These paramagnetic compounds have been isolated as tetrafluoroborates[80].

The formation of radical-anions in the electrochemical reduction of clusters has been reported. Radical-anions have been generated from iron carbonyls and also from their ruthenium and osmium analogues[81]:

$$[Fe(CO)_{12-n}L_n]^{\bullet-}$$

L = PPh_3, P(OMe)$_3$, P(OPh)$_3$, etc.

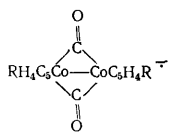
†In the formula below DME = 1,2-dimethoxyethane and MTHF = 2-methyltetrahydrofuran (Ed.of Translation).

The radical-anions of a tricobaltcarbon cluster have been obtained by electrochemical reduction[82]:

$$YCCo_3(CO)_9 \xrightarrow{+e} [YCCo_3(CO)_9]^{\cdot-} ;$$
$$Y = H, Me, Et, F, CF_3, CF_3CH_2, Cl, Br, Ph, p\text{-}FC_6H_4, COOH, p\text{-}HOC_6H_4, Me_3Si, \alpha\text{-}C_{10}H_7 .$$

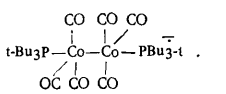
The radical-anions produced are relatively stable and the g-factors are 1.9800–2.0210. The unpaired electron interacts with the substituent Y (a_H = 10 G, a_F = 10.8 G) and also with the three equivalent ^{59}Co nuclei (I = 7/2), which leads to the appearance of 22 lines in the EPR spectrum with the constants $a_{^{59}Co}$ = 34.2–37.1 G.

The preparation of dinuclear cobalt radical-anions has been described[83]:



$$R = H, COOMe, Si(Me)_3, Si(Ph)_2Me, CH_2COOMe .$$

Complexes of another type with tri(t-butyl)phosphine ligands have the following structure[84]:



It has been suggested[84] that the unpaired electron occupies the Co–Co σ^* orbital, involving at the same time the P–Co–Co–P chain of atoms. The uniform distribution of the unpaired electron density over the two Co atoms makes it possible to treat such a dinuclear paramagnetic complex either as a compound with "mixed" valence metal species $Co^0 - Co^+$ or as formally a compound of +0.5-valent cobalt[83]. In all probability both these hypotheses are arbitrary and are most probably concerned merely with terminology. Evidently the immediate ligand environment also participates in the distribution of spin density[85]:

$$[X_2Co_2(CO)_6]^{\cdot-}$$
$$X = H_2C_2, t\text{-}Bu_2C_2, Ph_2C_2, Me_2C_2SiMe_3,$$
$$PhC_2SiMe_3, CF_3C_2SiMe_3, (CF_3)_2C_2, P_2, As_2;$$
$$a_{^{59}Co} = 2.37\text{–}2.88 \text{ G}, \quad a_P = 3.74 \text{ G}, \quad a_{As} = 2.12 \text{ G}.$$

One of the common methods of generating free radicals is homolytic bond dissociation. This method is suitable for the preparation of paramagnetic products on ultraviolet irradiation of dinuclear complexes of transition metals[86]. The photolysis of bis(tributylphosphine)dimanganese octacarbonyl $Mn_2(CO)_8(PBu_3)_2$ (the reaction is carried out in the presence of an excess of tributylphosphine) or tris(triethoxyphosphino)dimanganese heptacarbonyl $Mn_2(CO)_7[P(OEt)_3]_3$ in heptane with periodic removal of the CO evolved leads to the formation of paramagnetic intermediates. The EPR spectrum of the frozen irradiated solution indicates the presence in the system of the radical $Mn(CO)_3(PBu_3)_2^{\cdot}$ (its structure consists of a tetragonal pyramid with *trans*-axial phosphine ligands). The radical formed reacts slowly with the solvent, the reaction involving the abstraction of a hydrogen atom, which is typical for active free radicals. The formation of all possible products as a result of the free-radical reactions can be represented schematically as follows:

$$Mn_2(CO)_8L_2 \overset{h\nu}{\rightleftharpoons} 2Mn(CO)_4L^{\cdot} ;$$
$$Mn(CO)_4L^{\cdot} + L \rightleftharpoons Mn(CO)_3L_2^{\cdot} + CO ;$$
$$Mn(CO)_3L_2^{\cdot} + Mn(CO)_4L \rightleftharpoons Mn_2(CO)_7L_3 ;$$
$$2Mn(CO)_3L_2^{\cdot} \overset{h\nu}{\rightleftharpoons} Mn_2(CO)_6L_4 ;$$
$$Mn(CO)_3L_2^{\cdot} + HR \overset{h\nu}{\rightleftharpoons} HMn(CO)_3L_2 + R^{\cdot} .$$

The EPR spectrum has a hyperfine structure with two equivalent ^{31}P nuclei (I = 1/2, $a_{\parallel}$ = 20 G, $a_{\perp}$ = 19 G) and with one ^{55}Mn nucleus (I = 5/2, $a_{\parallel}$ = 54.1 G, $a_{\perp}$ = 35.7 G); the g-factor is 2.040. A similar situation is observed also for triethyl phosphite derivatives of manganese[86].

Apart from the photolytic method of bond dissociation with formation of free-radical species, thermolysis is also employed[87]. Thermal decomposition of manganese complexes leads, like photolysis, to paramagnetic products, whose formation can be demonstrated by the spin trapping method using t-butyl nitroxide as the trapping agent:

$$L_nM\text{—}ML_n \rightleftharpoons 2^{\cdot}ML_n; \quad {}^{\cdot}ML_n + R\text{—}N{=}O \rightarrow R\text{—}\underset{\underset{O}{|}}{N}\text{—}ML_n$$
$$R\text{—}N\text{—}ML_n \rightarrow \text{decomposition products;}$$
$$M = Mn, \ R = t\text{-}Bu, \qquad L = PPh_3, CO, PX_3, X = OMe, Et, Me, m\text{-}, p\text{-}MeC_6H_4, OEt .$$

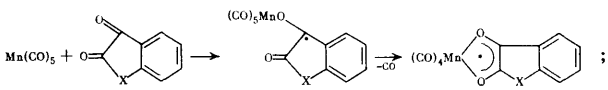
It is sometimes possible to detect the intermediate free radical, as, for example, in the case of triphenylphosphine-manganese tetracarbonyl:

$$Mn_2(CO)_8(PPh_3)_2 \rightleftharpoons 2^{\cdot}Mn(CO)_4(PPh_3)$$
$${}^{\cdot}Mn(CO)_4(PPh_3) + ON\text{—}Bu\text{-}t \rightarrow (PPh_3)(CO)_4Mn\text{—}\underset{\underset{O}{|}}{N}\text{—}Bu\text{-}t.$$

Lines due to the hyperfine interaction with the ^{55}Mn, ^{31}P, and ^{14}N nuclei are recorded in the EPR spectra. Metal carbonyls of the type $M_2(CO)_{10}$, where M = Mn or Re, have been considered in some cases[88].

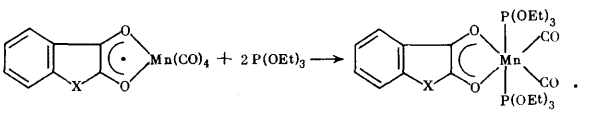
The irradiation of metal decacarbonyls in the presence of 1,2-dicarbonyl compounds[89] results in the formation of products of the addition of free radicals to diketones:

$$Mn_2(CO)_{10} \rightleftharpoons 2^{\cdot}Mn(CO)_5 ;$$

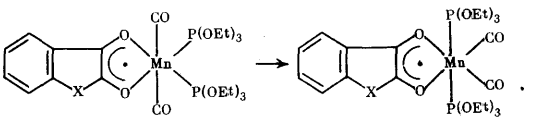


$$X = CO, NH, O, S .$$

The interaction of the resulting paramagnetic chelate with phosphines yields products of further reactions, but the paramagnetism of the molecule is maintained, an additional hyperfine interaction with the ^{31}P nuclei of the triethylphosphine ligands being observed:

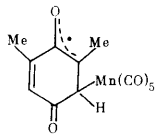


The authors[89] suggest that *cis–trans* isomerisation takes place in paramagnetic complexes of this type:

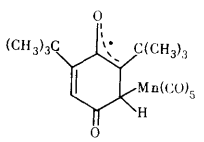


Chelates of the above type will be described below. The interaction with quinones and α-diketones of free metal-centred radicals, formed as a result of the thermal or

photolytic cleavage of the metal–metal bond in $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $(Me)_3SnMn(CO)_5$, and $Me_2Sn[Mn(CO)_5]_2$ has been thoroughly investigated by EPR.[90] Dimethylbenzoquinone, phenanthrenequinone, etc. have been used as the trapping agents. The differences between the structures of the quinones employed have a significant influence on the nature of the paramagnetic products formed. When *para*-quinones are used, the compounds formed can be regarded as organometallic σ-radicals with a paramagnetic fragment of the allyl type in the ligand:

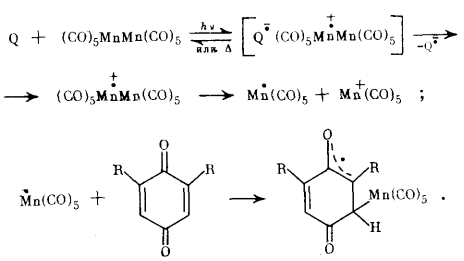


$a_H(Me) = 5.52$ G
$a_H(Mn) = 1.51$ G

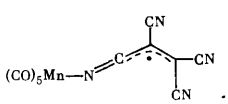


$a_H(Mn) = 3.38$ G .

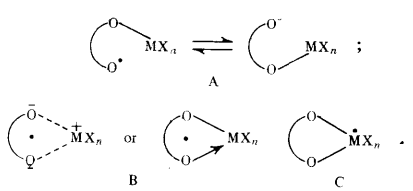
The following scheme for the formation of these paramagnetic species has been proposed[90]:



An analogous mechanism describes the reaction of $Mn_2(CO)_{10}$ with tetracyanoethylene, which results in the formation of an iminotricyanoallyl radical[91]:

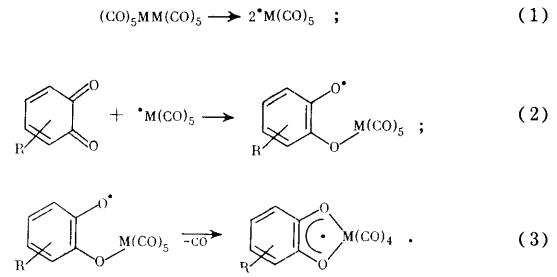


When the metal carbonyl dimers interact with *ortho*-quinones, it is necessary to consider in this instance several probable structures of the products formed[92]: structures of the phenoxy-type with localisation of the organometallic fragment at one of the oxygen atoms (A), a structure of the semi-quinone or chelate type (B), and a metal-centred radical (C):



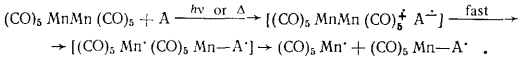
The addition of the fragment $^{\bullet}M(CO)_5$, formed on dissociation of the initial dimer, leads to structure (A), which is stable only at a low temperature. Slight heating results in the elimination of one CO group and the EPR spectra indicate the formation of structure (B), characterised by a symmetrical distribution of the spin density and a hexacoordinate manganese atom. The free radicals corresponding to structure (B) have been postulated for a series of quinones[93].

Overall, the reaction of dinuclear metal carbonyls with *ortho*-quinones can be represented by the following chain of transformations:

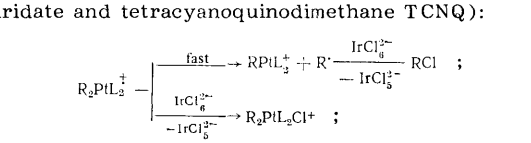


The activation energy for the unimolecular reaction (3) (17.3 kcal mol^{-1}) and the rate constant ($k_{-20^\circ} = 0.07$ s^{-1}) as well as all the spectroscopic characteristics of the primary [reaction (2)] and secondary [reaction (3)] radicals have been published[92].

If homolysis does not precede the formation of the reaction products, it is possible to postulate a reaction pathway[94] where the interaction of $M_2(CO)_{10}$ with the acceptor A takes place in the first stage via one-electron transfer and is followed by a rearrangement in a cage:

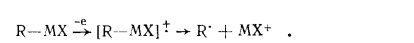


In the study of oxidation-reduction processes in organometallic chemistry, the problem arises of the formation of intermediate paramagnetic products and their subsequent reactions. A mechanism has been proposed[95] for electron transfer in the reactions of organoplatinum compounds having a Pt–C σ-bond with one-electron acceptors (hexachloroiridate and tetracyanoquinodimethane TCNQ):

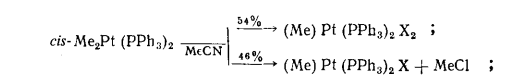


The ease of one-electron oxidation decreases in the sequence $Et_2Pt(PMe_2Ph)_2 > Me_2Pt(PMe_2Ph)_2 > Et_2Pt(PPh_3)_2 > Me_2 . Pt(PPh_3)_2$.

The oxidation of R_2PtL_2 by TCNQ results in the formation of a radical pair; the TCNQ radical-anion is manifested in EPR spectra. Further reactions follow after the emergence of the radicals from the cage. Overall, the picture is identical with that in the decomposition of organometallic compounds of non-transition metals (Mg, Hg, Sn, Pb):[96]



A characteristic feature of transition metal complexes is their ability to undergo a change in coordination number after a change in the state of oxidation. For this reason, there is a possibility also of another pathway involving transformation into quadrivalent platinum compounds; the two possibilities are approximately equivalent for *cis*-dimethylbis(triphenylphosphine)platinum:



In contrast to the preceding example, dialkyl(bipyridyl)-iron gives rise on oxidation with bromine to a mixture of hydrocarbons—the products of the disproportionation or

dimerisation of the radicals R$^{\cdot}$:[97]

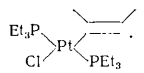
$$\left.\begin{matrix} R \\ R \end{matrix}\right\rangle Fe(bipy)_2 + Br_2 \left\langle \begin{matrix} \longrightarrow R{-}R + Fe(bipy)_2 \\ \longrightarrow 2RBr + FeBr_2(bipy)_2 \end{matrix} \right. ;$$

In this case the coordination number of iron atoms diminishes.

Aryl compounds of nickel decompose with partial coordination of a solvent molecule:

$$Ar_2NiL_2 \xrightarrow{-e} Ar_2NiL_2^{+} + S \xrightarrow{fast} Ar_2NiL_2(S)^{+} \xrightarrow{slow} \text{products}.$$

The formation of the alkenebis(triethylphosphine)platinum chloride radical has been noted[98]:



Paramagnetic palladium complexes of the π-allyl type, which exhibit a high catalytic activity, have been described as intermediates in the hydrogenation of nitro-compounds[99].

Nowadays the EPR method is widely used in the study of the paramagnetic complexes formed in catalytic processes[100]. Transition metal derivatives can behave as initiators of radical reactions of organic halogeno-compounds[101]. At any rate it is evident that many reactions in organometallic chemistry can proceed via the formation of free radicals. We shall consider some further examples.

On the basis of the study of the kinetics of the formal oxidative elimination reaction, it has been postulated that radical-cations are formed from iron complexes as an elementary stage of the reaction[102]

$$[Fe(CO)_3L_2] + I_2 \rightarrow [Fe(CO)_3L_2]^{+} + I^{\cdot} + I^{-} ;$$
$$[Fe(CO)_3L_2] + I^{\cdot} \rightarrow [Fe(CO)_3L_2]^{+} + I^{-} \text{ etc.}$$

The radical-cations formed were investigated by EPR.[102] The changes in the characteristics of the EPR spectra as a function of the electron-donating properties of the ligand L, where L = PPh_3, $AsPh_3$, $PMePh_2$, $P(NMe_2)_3$, $P(OPh)_3$, or $Ph_2PCH_2PPh_2$, have been traced. In all cases the EPR spectra indicate the occurrence of a hyperfine interaction with two equivalent nuclei of the donor heteroatom (P, As). For a full identification of the intermediate, the radical-cation was obtained by specific electrochemical synthesis:

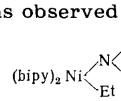
$$Fe(CO)_3L_2 \xrightarrow[\text{Pt electrode}]{-e} [Fe(CO)_3L_2]^{+} ,$$

and by interaction with a silver salt; in the presence of a halogen X the reaction proceeds with formation of a diamagnetic salt:

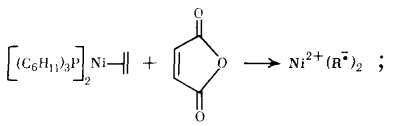
$$Fe(CO)_3L + AgPF_6 \xrightarrow{X_2} [Fe(CO)_3L_2][PF_6] .$$

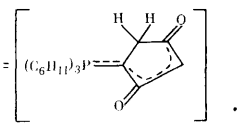
The paramagnetic radical-cation $[Fe(CO)_3L_2]^{+}$ formed has the structure of a trigonal bipyramid with the *trans*-configuration.

In the study of the mechanism of the aldol condensation and oxidation-reduction processes in the presence of organic σ-complexes of nickel with the aid of the spin trapping method[103], the involvement of free-radical intermediates of the following type was observed:

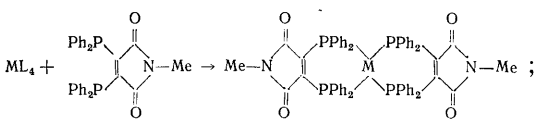


The interaction of ethylenebis(tricyclohexylphosphine)-nickel with maleic acid anhydride proceeds in an unexpected manner[104]. It has been suggested that intermolecular ligand exchange (the replacement of ethylene by the anhydride in the coordination sphere of the metal) results in further reactions with formation of a radical-ion salt (see below). The description of the compound obtained as a complex with a radical-anion ligand is based on spectroscopic data (EPR, ultraviolet spectroscopy). The doublet of triplets in the EPR spectrum characteristic of the given radical-anion is due to hyperfine interaction with the ^{31}P nucleus (a_P = 13.1 G) and two protons (a_H = 2.04 G). In the visible region the spectrum contains a band characteristic of the nickel(II) cation[104].





Radical complexes with maleic acid derivatives have been obtained also for palladium and platinum[105]. The interaction of zerovalent palladium, platinum, and nickel complexes with diphosphine derivatives of maleic anhydride leads to a diamagnetic complex of the zerovalent metal, stable in air, only in the case of nickel:



L=PPh_3, M=Pd, Pt; L=CO, M=Ni .

The palladium and platinum complexes are paramagnetic products unstable in air. It may be assumed that the ligand becomes a radical-anion as a result of electron transfer from the metal:

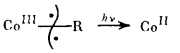
$$M^0(PP)_2 \rightarrow M^{I}[(PP)_2]^{-} .$$

Signals due to the hyperfine interaction with the two ^{31}P and N nuclei and the hydrogen atoms of the methyl group [a_P = 9.6 G, a_N = 3.0 G, and $a_{H(Me)}$ = 0.68 G] have been recorded in the EPR spectra. The HFI constants obtained are close to those for the paramagnetic salt $PP^{-}K^{+}$.

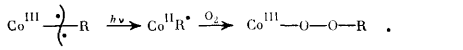
The photolytic interaction of cobalt complexes with sulphonyl chloride proceeds as the addition of the active free radical to the double bond, giving rise to paramagnetism in the ligand sphere of cobalt[106]:

$$RSO_2^{\cdot} + [R'R''C{=}CHCH_2CoL_2Py] \rightarrow$$
$$\rightarrow [RSO_2CR'R''CHCH_2CoL_2Py] \left\langle \begin{matrix} \rightarrow RSO_2CR'R''CH{=}CH_2 \\ \rightarrow [Co^{II}L_2Py] \end{matrix} \right. .$$

An interesting example of the homolytic cleavage of the metal–ligand bond is the anaerobic photolysis of derivatives of cobaltoxime via the mechanism[107]



In the presence of oxygen a peroxide is formed in this reaction[108]:

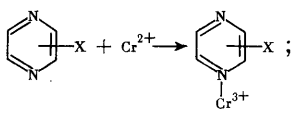


Paramagnetic organometallic compounds can also be formed as a result of interaction with an organic free radical[109]:

$$Ag + {}^{\cdot}CH_2CN \rightarrow Ag^{-}CH_2CN ;$$
$$Ag + {}^{\cdot}CH_2OH \rightarrow Ag^{-}CH_2OH ;$$
$$Ag^{+} + CH_3CN^{\cdot-} \rightarrow Ag{-}C(CH_3){=}N^{\cdot} .$$

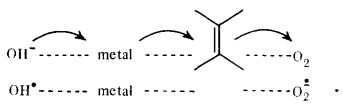
There is also a possibility of the reduction of a ligand to a

paramagnetic species with its simultaneous coordination to the reductant metal[110]:



X = Me, Cl, COOH, $CONH_2$.

An extremely interesting study[111] of metal-catalysed photochemical organic reactions of olefins involved simultaneously several important problems. A chain mechanism of the intramolecular electron transfer was postulated. The donor is the hydroxide ion and the final acceptor is oxygen:



Electron transfer proceeds via a chain with participation of a transition metal atom (Fe). The development of studies of this type can apparently elucidate the mechanisms of enzymatic oxidation reactions.

Thus a fairly large number of paramagnetic complexes are known whose magnetic properties are determined either by the electronic configuration of the central ion or by the appearance of an unpaired electron as a result of an oxidation-reduction process. An odd number of electrons in the *d* and *f* levels of the central ion in the first group of compounds does not cause qualitative changes in the nature of the metal–ligand bond and the structure of the complex and in essence such compounds differ little from their diamagnetic analogues. As regards charged paramagnetic compounds, it is rarely possible to obtain stable radicals; all the measurements are made at low temperatures and it is rarely possible to isolate the product.

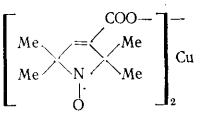
The essential requirements are, firstly, a relative simplicity of the synthesis and, secondly, the possibility of the preparative isolation of stable paramagnetic compounds. The development of the chemistry of free radicals made it possible to satisfy these requirements, which permitted the employment of stable organic radicals as ligands. Mainly stable nitroxy- and *ortho*-semiquinone paramagnetic ligands are used nowadays in the chemistry of transition metal complexes. In addition, a large number of examples of variable-valence metal complexes with nitric oxide[112] or its derivatives, coordinated via the N–O bond, have been described in the literature[113–124].

IV. STABLE NITROXY-RADICALS IN TRANSITION METAL COMPLEXES

The class of nitroxy-radicals is of considerable interest in view of their high stability[125]. These radicals have found extensive applications as spin labels and paramagnetic probes for the study of molecular dynamics and the structures of liquids in polymeric formations, biological systems, etc.[126].

Nitroxy-radicals are π-electron radicals. In aliphatic nitroxy-radicals the unpaired electron is localised almost wholly in the N–O fragment; after the introduction of aromatic substituents (R^1, R^2 = Ar), the spin density on the N and O atoms diminishes owing to the establishment of a conjugation system and a considerable proportion of the unpaired electron density is transferred to the aromatic rings[127,128].

The synthesis of the copper salt of 3-carboxy-2,2,5,5-tetramethylpyrrolin-1-yloxy-radical was described for the first time in 1966:[129]



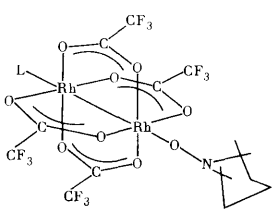
This compound was isolated in the form of a stable crystalline substance. In the solid state the salt does not give rise to an EPR signal, while in solution (in water and ethanol) a weak signal can be recorded.

Thus it became possible to synthesise from derivatives of nitroxy-radicals complexes with ligands known to be paramagnetic beforehand. Nitroxy-radicals are, in principle, ambifunctional ligands and the complexes based on them can be divided into two classes in accordance with the type of ligand–metal coordination:

(1) Coordination via the N–O group carrying the unpaired electron; this leads to a spin–spin interaction between the nitroxy-fragment and the metal ion, provided that its isotope is paramagnetic.

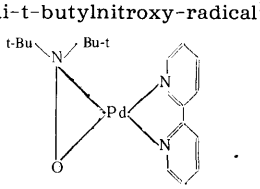
(2) Coordination via other functional groups of the ligand which show a greater tendency towards complex formation than the N–O group; there is then a possibility of exchange interactions of the radical centres with one another and with the metal ion.

The first case is of no particular interest because in compounds of this kind there is a possibility of the disappearance of paramagnetism; however, for example, in the EPR spectrum of the product of the addition of the nitroxy-radical to the rhodium trifluoroacetate dimer[130], the signal is split owing to the interaction with the ^{103}Rh nucleus ($I = 1/2$, $a_{Rh} = 1.7$ G).



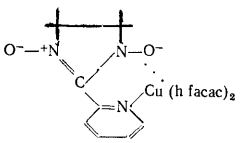
In this case the unpaired σ-electron is donated by the nitroxy-group to the d_{z^2} orbital of rhodium and there is a reverse interaction of the d_{xy} orbital of the rhodium atom with the π* orbital of the NO group carrying the unpaired electron.

An unusual three-membered ring is formed in the complex of palladium with the di-t-butylnitroxy-radical[131]:



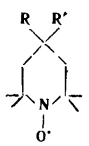
Complexes of other variable-valence metals have also been described[131–135]. It is difficult to draw a sharp boundary between compounds of the first and second types. There is a possibility of instances of coordination via a functional group accompanied by the simultaneous interaction of the metal ion with the nitroxy-fragment, which is in many respects determined by the structure of the complex. It has been shown[136–139] that the geometry of the complex influences the nature of the bond. In the series of compounds of copper, manganese, and vanadium with α-, β-,

and γ-pyridylnitronyl nitroxide, copper or vanadyl α-pyridyl-nitronylnitroxide bishexafluoroacetylacetonate is diamagnetic:



The occurrence of additional coordination of this type can be accounted for by intermolecular electron transfer from the $d_{x^2-y^2}$ orbital of copper or the d_{xy} orbital of vanadium to the $2p\pi$ orbital of the nitroxy-group and is based on the energies of the singlet–triplet cleavage.

Table 1. Transition metal complexes of the type ML_nX_m containing the iminoxy-fragments

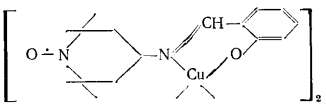


R, R'	ML_nHal_m	References
R=R'=H	CoL_2I_2	[141]
»	$(PdLCl)_2$	[141]
»	$CuLCl_2$	[141]
»	[Rh(hfacac)$_2$]L	[130]
R=H, R'=NH_2	CoL_2I_2	[141]
»	PdL_2Cl_2	[141]
»	CuL_2Cl_2	[141]
»	NiL_2Hal_2	[142]
»	PtL_2Hal_2	[142]
»	ZnL_2Hal_2	[142]
R=NH_2, R'=COOH	CoL_2	[141]
»	$NiL_2\cdot 2H_2O$	[141]
»	PdL_2	[141]
»	$PtL_2\cdot 2H_2O$	[141]
»	CuL_2	[141]
»	ZnL_2	[141]
R=H, R'=COOH	ML_2, where M=Cu, Co, Pd, Pt, Zn, Ni	[142]
R=H, R'=—N=CH—CH=N—	$PdLCl_2$	[141]
»	$(CuLCl)_2$	[141]
R=H, R'=—N=CH—C_6H_4—O	CuL_2	[143, 145]
»	FeL_3	[143, 145]
»	CoL_2	[143, 145]
»	NiL_2	[143, 145]
»	ZnL_2	[143, 145]
R=H, R'=O—C(=S)—S—	ZnL_2	[146]
»	HgL_2	[146]
»	CoL_2	[146]
»	NiL_2	[146]
R, R'=N—N=C—NH_2 (S)	CoL_2	[144]
»	NiL_2	[144]
»	CuL_2	[144]
»	ZnL_2	[144]
R=H, R'=—N=C—(C=N→)	$CuL(hfaa)_2$	[147], 148]
R=H, R'=—NH—C(=O)—R*	CuL	[151]
R=Ph, R'=H	$[PdLX]_2$	[151]

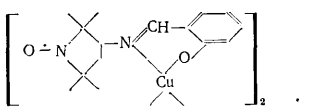
*R_p = porphyrin residue.

In the zinc compounds with a similar mode of coordination there is no direct interaction with the radical centre[140]. There are more numerous examples of transition metal complexes with coordination via the functional groups of the substituents in the radical ligands. In the main these are derivatives of 2,2,5,5-tetramethylpiperidin-1-yloxy-, 2,2,5,5-tetramethyl-Δ^3-imidazolin-1-yloxy-, and 2,2,5,5-tetramethylpyrrolin-1-yloxy-radicals. The types of complexes based on the piperidinyloxy-radical are presented in Table 1.

The magnetic properties of complexes with paramagnetic ligands have been investigated by determining the magnetic susceptibilities and by EPR.[149,150]. The magnetic susceptibility of the copper complex of the Schiff base[152]

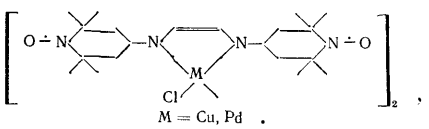


indicates the presence of three unpaired electrons in the molecule and is equal to the sum of the susceptibilities of three non-interacting or weakly interacting spins. However, the analogous complex differing by only one methylene unit in the ring of the radical proved to be diamagnetic in the crystalline state, which the authors explain by the formation of the coordinate bond $NO^{\cdot} \rightarrow Cu^{2+}$ in the polymeric crystal lattice:



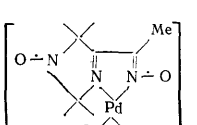
The EPR spectra of the solutions indicate the occurrence of weak exchange interactions in the radical centres and Cu^{2+} ions.

The nickel(II), palladium(II), and zinc(II) complexes of the 4-amino-4-carboxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical give rise to triplet spectra typical for nitroxy-radicals[141], which do not differ significantly from the spectra of the free radicals. A change of temperature also does not affect the nature of the spectra. For the palladium(II) and copper(II) complexes of the biradical ligand



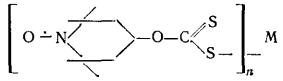
M = Cu, Pd .

an EPR spectrum characteristic of free radicals with a weak exchange interaction between the radical centres was obtained: $I < a$, where a = 15 G is the constant for the hyperfine interaction of the unpaired electron in the ^{14}N nucleus and I the exchange interaction energy. The exchange interactions in dimeric complexes are manifested spectroscopically by additional lines in the EPR spectrum relative to the initial ligand. These data make it possible to confirm the structure of the dimeric complex with the aid of a spin label[153]:



For the cobalt(II) and palladium(II) complexes of the 4-amino-2,2,6,6-tetramethylpiperidin-1-yloxy-radical, it is possible to observe in the EPR spectrum a quintet corresponding to strong exchange between the radical centres, i.e. $I \gg a$. In the analogous copper(II) complex the unpaired electron of the radical ligand interacts with the copper ion, to which corresponds a broad signal in the EPR spectrum[154].

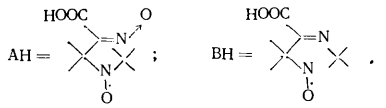
For the complexes with the paramagnetic xanthate ligands[146]



M = Zn (II), Hg (II), Co (III), Ni (II) ,

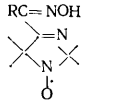
the g-factors are in the range 2.0075–2.0089, which differs little from the g-factors of the nitroxy-radicals. This can be explained by the fact that in the given complexes the metal ions interact only weakly with the radical centres. At room temperature the EPR spectra of the solutions are characterised by a triplet (a_N = 15–16 G). A weak intramolecular spin exchange between two radical centres is exhibited for zinc and mercury (the intensity of the biradical components is ~5% of the main signal).

Transition metal acetates containing paramagnetic fragments of the following type have been obtained[155]: $CoA_2.2H_2O$, $NiA_2.2H_2O$, $CuA_2.2H_2O$, $ZnA_2.2H_2O$, $PrA_3.3H_2O$, $EuA_3.2H_2O$, $CoB_2.4H_2O$, $CuB_2.4H_2O$, $ZnB_2.4H_2O$, and PdB_2.



A single broad line with a g-factor equal to the mean of the g-factors of the metal ion and the ligands is observed in the EPR spectra of the copper(II) complexes. In the copper(II) and nickel(II) compounds there is an exchange interaction between the paramagnetic centres; the zinc(II) and palladium(II) complexes give rise to quintets typical for biradicals; in praseodymium(III) and europium(III) acetates there is no exchange interaction between the paramagnetic centres, i.e. the usual triplet is observed in the EPR spectrum (a_N = 15.1 G).[156,157]

The 4-hydroxyiminomethyl-2,2,5,5-tetramethyl-Δ^3-imidazolin-1-yloxy-radical forms chelate rings with the copper(II), nickel(II), palladium(II), cobalt(III), and zinc(II) ions via the oxime group and the electron-donating ring nitrogen atom:



R = H, Me .

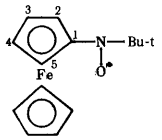
A quintet typical for biradicals has been recorded in the EPR spectra of such complexes[158,159].

The EPR spectra of solutions of the analogous copper(II), nickel(II), cobalt(III), and palladium(II) (R = Me) complexes[160] in chloroform have not been observed, which is a consequence of the strong exchange interaction between the metal ions and the paramagnetic ligands, which leads to a marked decrease of the electronic relaxation time. The EPR spectra of the cobalt(III) and palladium(II) chelates are quintets.

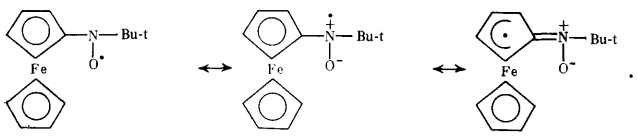
All the examples enumerated above permit the conclusion that there is only a weak interaction between the radical centre and the metal ion in complexes of the above type or that such interaction is altogether absent, which implies that the paramagnetic ligand hardly introduces any changes into the usual complexes, be they acetates, xanthates, or Schiff bases, and functions only as a paramagnetic label. This is due to the absence of a conjugation chain between the radical centre and the metal.

A completely different picture is observed in complexes in which the metal atom is involved in a conjugation chain with the paramagnetic fragment. Unfortunately such examples are extremely rare. However, it is clear that in cases of this kind the unpaired electron interacts with the orbitals of the metal atom.

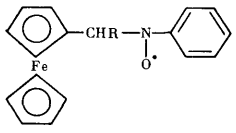
In the stable nitroxyferrocenyl radical[161]



the spin density at the ^{14}N atom is smaller than in the di-t-butylnitroxy-radical ($a_{^{14}N}$ = 13.3 G) and the g-factor (2.0149 ± 0.0004) exceeds the g-factor for arylnitroxy-radicals (2.006). The HFI constant (0.8 G) corresponding to the second and fifth ring protons is smaller by a factor of 2.5 than the HFI constant for the remaining protons ($a_{o\text{-}H} \cong$ 2.0 G) in the aryl fragment of the phenyl-t-butyl-nitroxy-radical (PTN). The following mesomeric structures have been proposed[161] taking into account conjugation:



The constants a_N = 10.9 G and a_H = 2.95 G have been obtained for the nitroxy-radical separated from the ferrocenyl substituent by a carbon atom[162]:

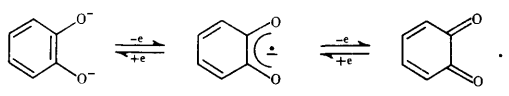


R = MeC_6H_4, Ph, Me .

V. TRANSITION METAL COMPLEXES WITH *ORTHO*-SEMIQUINONE LIGANDS

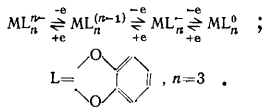
There has always been an extremely great interest in aromatic dicarbonyl compounds, starting with the first studies by Michaelis[163,164], who postulated the formation from quinones in biochemical reactions of the active forms of certain enzymes as radical species. Sufficient data concerning the role of quinone derivatives in oxidation-reduction enzymatic processes have now accumulated[165].

Compounds of the type of *ortho*-quinones[166] are characterised by the formation of the redox triad:

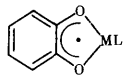


dianion *ortho*-benzosemiquinone *ortho*-benzoquinone

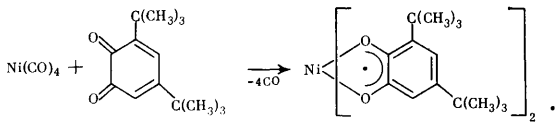
It was to be expected that a similar system, linked by one-electron transitions, is formed also by transition metal chelates:



In this series a complex is formed with the unpaired electron in the ligand:



The synthesis of a nickel complex by the reaction of nickel tetracarbonyl with 3,5-di-t-butyl-1,2-benzoquinone was reported in 1966:[167]

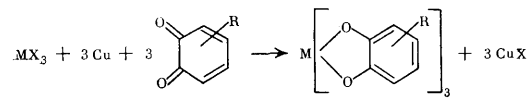


Chromium, molybdenum, and tungsten complexes based on *o*-chloranil were obtained in 1974.[168-171]

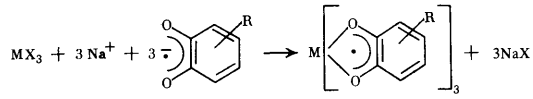
The chemistry of transition metal complexes with paramagnetic *ortho*-semiquinone ligands was developed to the greatest extent in the studies by Razuvaev, Abakumov, and coworkers[172-177]. Copper, silver, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, iron, gallium, gadolinium, palladium, and nickel complexes with *ortho*-quinone fragments were obtained[173-177].

The methods of synthesis of complexes of tervalent metals can be combined in the following groups.

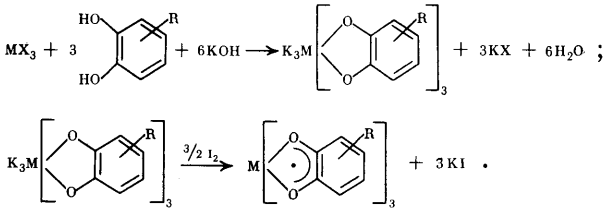
1. The interaction of metal halides and *ortho*-quinones in the presence of metallic copper:



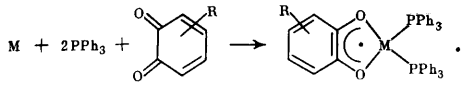
2. The reaction of transition metal halides with sodium or thallium *ortho*-semiquinolates:



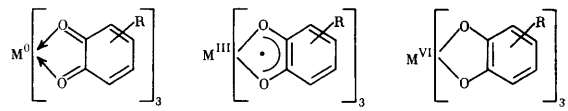
3. The exchange reaction between a transition metal salt and the catechol dianion:



4. The monoligand copper and silver complexes can be obtained by the direct interaction of the quinone and the metal in the presence of a stabilised ligand, for example, triphenylphosphine[176]:



Complexes of different transition metals have been synthesised in this way. Of the three possible types of structures of the above complexes, structure B is believed to be closest to reality[176]:



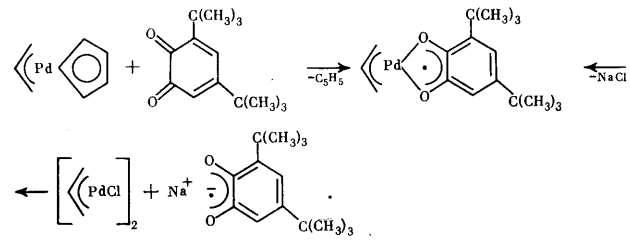
A-(quinone) B-(semiquinone) C-(catecholate)

M = Cr, Mo, W .

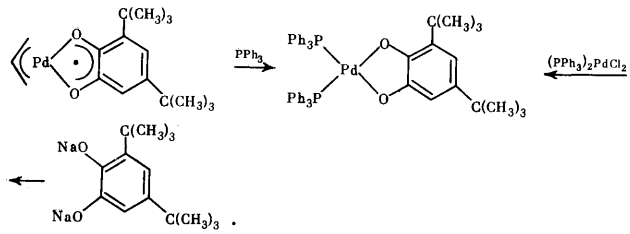
The term "quasi-radical ligands" has been proposed for the ligands of this type, implying the possibility of exchange interactions between the paramagnetic fragment and the metal ion[176].

In the general case the distribution of spin density in the paramagnetic complex does not differ significantly from that in the *ortho*-semiquinone radical-anion. In the presence of stabilising ligands ER_3 (where E = P or As and R = Ph, Et, or OEt) in the molecule of the complex, the unpaired electron is seen to interact not only with the magnetic isotopes of the metal ion but also with the ^{31}P and ^{75}As nuclei of the extraneous [sic] ligand (a_P = 12–20 G).[169]

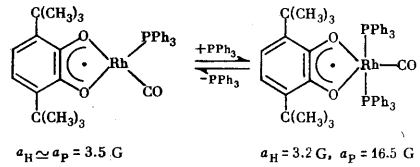
For example, the allyl group can serve as an extraneous ligand:



However, in this case it was not possible to observe the hyperfine interaction of the unpaired electron with the allyl fragment[175,176] owing to the great width of the HFS lines in the EPR spectra. The allyl complex can be converted into the corresponding triphenyl phosphine derivative:



The possibility of reversible conversion into a complex with a pentacoordinate rhodium atom (trigonal bipyramid) has been demonstrated in relation to the square-planar rhodium complex[177]:



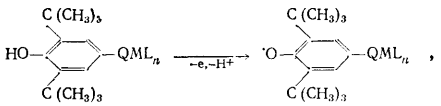
$a_H \simeq a_P$ = 3.5 G a_H = 3.2 G, a_P = 16.5 G

All the paramagnetic complexes obtained are relatively stable and they are also stable in the presence of oxygen[178,179].

Thus the data obtained demonstrate the possibility of introducing free-radical *ortho*-semiquinolate species into a molecule of the transition metal complex.

VI. PHENOXY-RADICALS IN PLATINUM METAL COMPLEXES

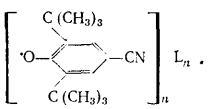
Another approach to the synthesis of paramagnetic complexes was followed when a series of stable phenoxy-radicals were used. A series of complexes based on sterically hindered phenols were obtained, their one-electron oxidation resulting in the formation of metal-containing free phenoxy-radicals[180–186]:



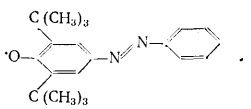
where Q is the coordinating group and M = Pd, Pt, or Ph.

The compounds obtained can be divided into several groups in terms of the type of the metal–paramagnetic ligand bond (L = Cl, Br, I, PPh_3, acac, THF, or π-C_5H_5).

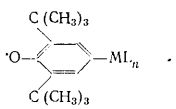
I. *n*-Donor coordination:



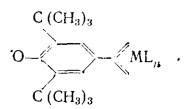
II. σ-Bond + *n*-donor coordination:



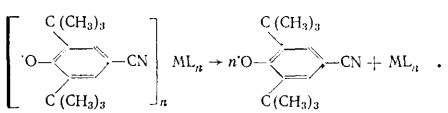
III. σ-Bond:



IV. π-Bond:



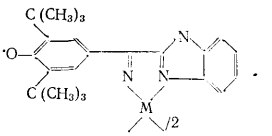
Group I free radicals are unstable and dissociate with liberation of the stable cyanophenoxy-radical into the solution:



The EPR spectra of Group II complexes are isotypical[180]; a hyperfine structure is observed, which can be explained by the interaction of the unpaired electron with the *meta*-protons of the phenoxy-ring (a_H = 1 G) and with two ^{14}N nuclei (I = 1, a = 2 G). At the same time the radical corresponding to the initial ligand is extremely unstable and decomposes rapidly even at 20 °C with liberation of molecular nitrogen, diphenoquinone, biphenyl, and their reaction products[187,188]. Its EPR spectrum is poorly resolved and yields virtually no information.

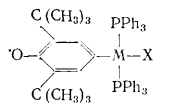
The fairly high stability of the organometallic azophenoxy-radicals in the range between −40° and +40 °C implies that the metal–carbon σ-bond, stabilised by the coordination to the nitrogen atom, is fairly stable, despite the presence of a paramagnetic fragment in the ligand, i.e. *ortho*-metallation and *n*-donor coordination (the formation of an organometallic ring) increase significantly the stability of the organic free radical. Furthermore, on formation of complexes, the spin conductivity of the azo-group increases, since in the ligand free radical the −N=N− unit is "non-conducting".

Phenoxy-radicals containing a heterocyclic fragment are also relatively stable[186]:



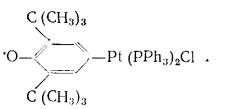
A triplet of triplets is observed in the EPR spectrum of the palladium(II) complex (a_H = 1.7 G, a_N = 4.8 G, a_{Pd} = 24 G); a septet is characteristic of the platinum(II) complex (a_H = 1.7 G, a_N = 3.4 G, a_{Pt} = 21.5 G).

The σ-bonded organometallic phenoxy-radicals obtained proved to be extremely stable[183]:



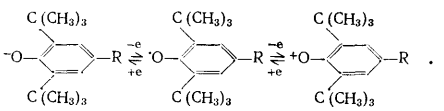
X = Cl, Br, I; M = Pd, Pt .

Their concentration does not decrease when the temperature is raised to 100 °C, they are stable for a long time in solutions, and they can be stored in evacuated bulbs for an unlimited period. A phenoxy-radical containing a platinum atom has been isolated in the solid state:



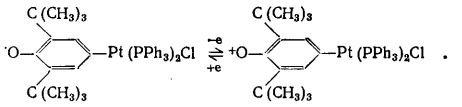
Its infrared spectrum does not contain the band corresponding to the vibrations of the OH bond and the band due to the stretching vibrations of the >C=O group appears in the region of 1640 cm^{-1}. The platinum-containing radicals are more stable than their palladium analogues. Depending on the nature of the halogen, the stability of the radicals decreases in the sequence Cl > Br > I. The unpaired electron interacts with the *meta*-protons of the phenoxy-ring, with the magnetic isotopes of the transition metal, and also with two equivalent ^{31}P nuclei (Table 2), which indicates a *trans*-geometry of the complex. The constants for the hyperfine interaction with the *meta*-protons in the palladium and platinum derivatives indicate the electropositive nature of the organometallic group. The high constant for the hyperfine interaction with the palladium and platinum nuclei and with the phosphorus nuclei of the triphenylphosphine ligands indicate a significant involvement of the *d* orbitals of the transition metal and the *p* orbitals of the phosphorus atom of triphenylphosphine in the distribution of spin density.

The free radicals exhibit a dual reactivity: in reactions with reductants they accept one electron and in reactions with oxidants they give up one electron:



The reduction of phenoxy-radicals to phenoxide ions constitutes a fairly trivial fact. Oxidation with formation of the phenoxylium cation has been described only for a limited number of organic derivatives[189,190]. In relation to stable σ-bonded derivatives, it proved possible to observe the reducing properties of organometallic radicals. The platinum-containing phenoxy-radical is oxidised by vanadyl chloride or tetracyanoquinodimethane to the phenoxylium

cation with retention of the metal–carbon bond:



Initially one observes in the EPR spectra a superposition of two spectra—that of the initial phenoxy-radical and that of the radical-anion $TCNQ^-$. After a time, the signal of the initial phenoxy-radical disappears and the spectra show only the signal due to $TCNQ^-$. As the reductant is added, the signal of the radical-anion $TCNQ^-$ gradually disappears and the signal of the initial platinum-containing phenoxy-radical takes its place, which demonstrated the reversibility of the reaction.

Table 2. The EPR parameters of the σ-bonded derivatives of phenoxy-radicals (toluene, 25 °C).[183]

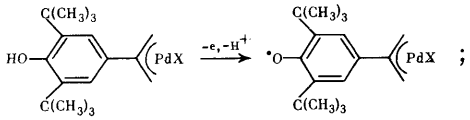
M	α*, %	I	a_H, G	a_{31P}, G	a_M, G	g-factor
Pt	33.7	1/2	1.2	16.0	94.0	2.0079
Pd	22.2	5/2	1.5	18.7	5.15	2.0051

*Natural abundance of the magnetic isotope.

Table 3. The EPR parameters of the π-allylpalladium-containing phenoxy-radicals (toluene, 25 °C).[184]

X	a_H^{meta}, G	a_H^{all}, G	a_{Pd}, G	g-factor
Cl	1.8	0.9	12.2	2.0051
Br	1.8	0.9	11.5	2.0057
I	1.8	0.9	10.3	2.0076
PPh_3Cl	1.8	0.9	9.2	2.0052
acac	1.8	0.9	—	2.0043
C_5H_5	1.6	0.8	5.4	2.0038

Phenolic π-allyl derivatives have been used to generate π-allylpalladium-containing phenoxy-radicals[184]:

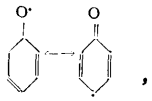


X = Cl, Br, I, PPh_3, acac, Cp .

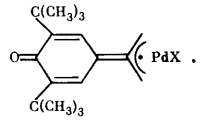
The spectroscopic parameters of the radicals obtained are presented in Table 3. The unpaired electron interacts with the *meta*-protons of the phenoxy-ring, with the protons of the terminal methylene groups of the allyl ligand, and with the magnetic palladium isotope ^{105}Pd. The last interaction results in the appearance at the edges of the main signal of satellite lines whose intensity is ~20 times lower than that of the main signal. Table 3 shows that, on passing from the chloride to the cyclopentadienyl derivative, the $a_{^{105}Pd}$ diminishes, the greatest effect being observed for the π-cyclopentadienyl ligand. In the square planar complexes this quantity diminishes monotonically with increasing bulk of the substituent at the palladium atom (Cl, Br, I, PPh_3). In the formally octahedral π-cyclopentadienyl derivative a more pronounced decrease of $a_{^{105}Pd}$ is observed. If $a_{^{105}Pd}$ is adopted as a measure of the delocalisation of the spin density, then its variation as a function of the group X will reflect the influence of the π-allylpalladium-containing group as a substituent in the *para*-position of the phenoxy-radical. The electronic characteristics of this group as a substituent in an aromatic ring are known[191].

A satisfactory linear dependence of $\delta_{^{19}F}$ and $a_{^{105}Pd}$ on the electronegativity of the ligand X ($r = 0.996$) has been observed for square planar complexes; the slope of the straight line $\rho = -7.162$ ($\Delta\rho = \pm 1.883$) indicates a greater influence of the ligands X on the distribution of spin density compared with their influence on the distribution of electron density. On passing to the formally octahedral π-allyl-π-cyclopentadienylpalladium complex[186], the linear relation is somewhat impaired ($r = 0.966$); the straight line is inclined still more steeply relative to the coordinate axis on which the values of a_{Pd} have been plotted. Thus the spin density is in some way redistributed over the metal atom in the π-cyclopentadienyl derivative, in which the electron density in the 2-position is significantly reduced as a consequence of the strong electron-donating influence of the ligand π-C_6H_5.

The parallel variation of the distributions of the electron densities in the compounds investigated is striking in both instances. As shown previously[191], the electronic effects can be transmitted between the benzene ring and the π-allyl ligand only via an inductive mechanism. The question arises whether one can assume that the transmission of spin density also involves an analogous mechanism. However, the role of the inductive effect in the distribution of electronic charge, at least in the phenoxy-part of the molecule, should be significantly smaller than the role of the conjugation effect[187–191]. It is necessary to elucidate how the charge density of the unpaired electron, delocalised to the *para*-position in the phenoxy-radical via the conjugation chain, is then redistributed to the π-allyl fragment,



and then further to the palladium atom (provided that further conjugation with the central carbon atom of the π-allyl ligand is impossible). In other words, there is no resonance structure of the type



The above question can be answered as a result of the following observation; in diamagnetic complexes the signals of the *syn*- and *anti*-protons of the π-allyl ligand are observed in the NMR spectrum for different field strengths as a consequence of the different degrees of shielding. In the EPR spectra of the corresponding free radicals a pattern is observed which indicates the equivalence of all four allyl protons (a quintet, $a_H = 1$ G). Thus the *syn-anti* exchange, leading to the equivalence of all the protons in the usual allyl complexes and observed on the NMR time scale either with increase of temperature or when the system

contains a strong electron-donating ligand, also occurs in the paramagnetic analogues under the usual conditions.

The equivalence of the four allyl protons observed on the EPR time scale following the transition from the diamagnetic to the paramagnetic system shows that the energy barrier in the intramolecular rearrangements in free radicals is lower than in the corresponding diamagnetic compounds. In other words, in paramagnetic complexes a reversible metallotropic rearrangement can take place much more readily:

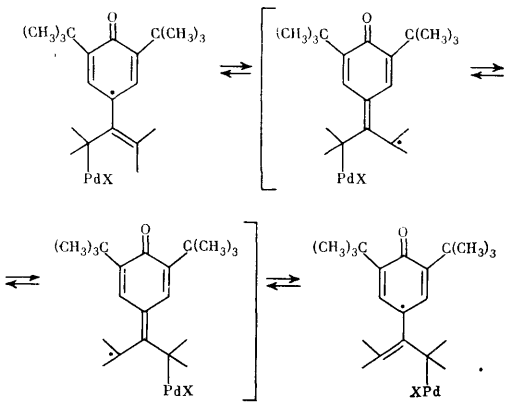


Table 4. Dependence of $a_{^{105}Pd}$ on the solvent (20 °C).[184]

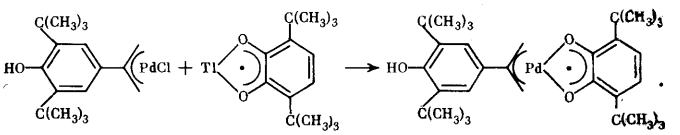
Solvent	$a_{^{105}Pd}$, G	Solvent	$a_{^{105}Pd}$, G
C_2H_5OH	14.6	Dioxan	13.2
$CH_3COC_2H_5$	13.6	Toluene	13.1

Table 5. Temperature variation of $a_{^{105}Pd}$ (toluene).[184]

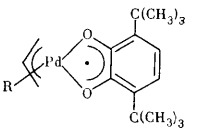
t, °C	20	0	−20	−40	−60
$a_{^{105}Pd}$, G	13.1	13.2	13.4	13.6	13.7

As a result of this, the system resembles the allyl compounds of non-transition metals, for which the decisive role of metallotropy has been demonstrated in dynamic processes, leading to the equivalence of the terminal hydrogen atoms[198].

The EPR spectra of the paramagnetic palladium complex (X = Cl) have been studied in different solvents (Table 4) and at different temperatures (Table 5). The equivalence of the four protons of the allyl ligand is maintained in all cases. Consequently the driving force of the rapid dynamic processes occurring in the paramagnetic allyl complexes is the delocalisation of the spin density over the entire molecule. The question arises whether the dynamic state of the allyl system is preserved also in the case where the paramagnetic fragment is not linked directly to the allyl ligand. A study was therefore made[184] by the EPR method of the interaction of the π-allyl complexes of palladium with thallium 3,6-di-t-butyl-*ortho*-semiquinolate:

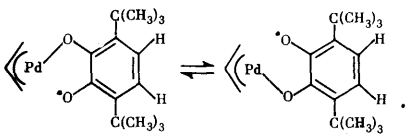


The unpaired electron interacts with two equivalent protons of the *ortho*-semiquinolate ring (a_H = 3.37 G), with the magnetic isotope ^{105}Pd (a_{Pd} = 2.35 G), and with two protons of the allyl fragment (a_H^{all} = 0.97 G). An analogous picture is observed also for other substituted π-allyl complexes.

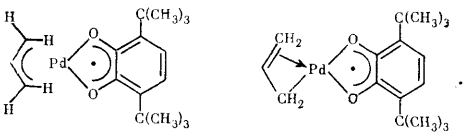


R = 2-H, 2-Ph, 2-$MeOC_6H_4$, 1-FC_6H_4 .

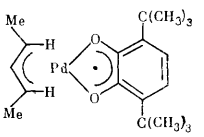
A triplet due to the two protons of the paramagnetic ligand and the two protons of the π-allyl ligand appears in all cases; each component of the triplet is split further into another triplet. The equivalence of the two protons in the *ortho*-semiquinolate ligand is a consequence of the rapid reversible migration of the palladium atom[199]:



The appearance in the EPR spectrum of the triplet due to the two equivalent protons of the π-allyl ligand can have two causes: firstly, the interaction of the unpaired electron solely with the *anti*-protons while retaining the π-allyl structure (A) and, secondly, the possibility of the freezing of the σ-structure (B):

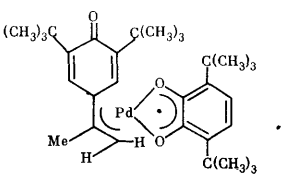


A 1,3-disubstituted allyl complex of the type



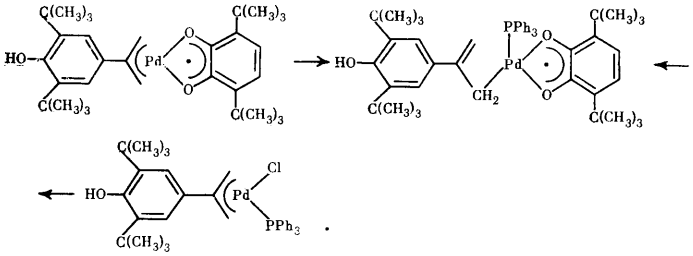
was used to solve this problem. The EPR spectrum of this radical contains a triplet caused by the interaction of the unpaired electron solely with the two *anti*-protons of the π-allyl ligand.

Analysis of the EPR spectra of an allyl complex with a quinonoid bond system leads to the same conclusion[185]:

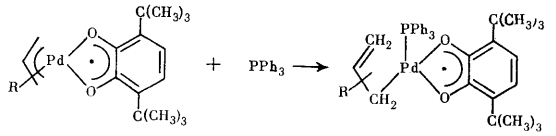


In this case the unpaired electron interacts only with one *anti*-proton of the allyl group and the HFI constant is ~0.5 G, which is smaller approximately by a factor of two than in all the cases described above[181,184].

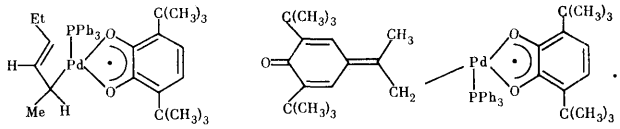
The formation of a σ-structure in the systems investigated was observed only in the presence of triphenylphosphine; the σ-complex was isolated on a preparative scale and has been obtained by specific synthesis:



An analogous transition, which led to an overall rearrangement of the bond system, has been studied spectroscopically for complexes with different substituents in the π-allyl ligand:



For R = 2-H, 2-C_6H_5, 2-$MeOC_6H_4$, or 1-FC_6H_4, a triplet due to the two protons of the terminal carbon atom is observed (a_H = 0.4–0.6 G); in addition the unpaired electron interacts with the ^{31}P nucleus ($a_{^{31}P}$ = 2.55 G). A doublet due to a single proton (a_H = 0.5 G) has been recorded in the EPR spectra of 3-ethyl-1-methylallylpalladium *ortho*-semiquinolate, and a triplet due to two protons (a_H = 0.6 G) has been observed in the spectrum of the quinonoid complex[184]:



Thus the nature of the processes occurring in paramagnetic π-allyl complexes is determined to a significant extent by the position of the free-radical ligand relative to the allyl group. When the unpaired electron appears directly in the allyl ligand, the system becomes dynamic; on the other hand, for systems with an extraneous ligand, carrying the unpaired electron, the π character of the ligand–metal bond is retained, but the π–σ transition is significantly facilitated compared with the diamagnetic ligand corresponding to the allyl compounds.

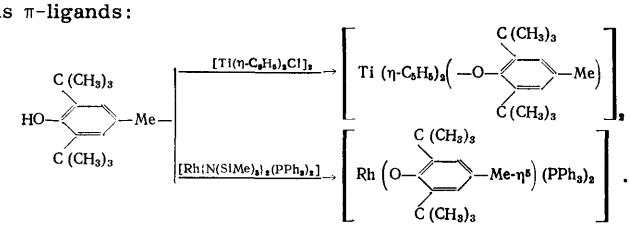
Yet another fact drew attention in the study of the free radical generated by the oxidation of π-allylpalladium-substituted phenols. The radical corresponding to the initial ligand, namely 2,6-di-t-butyl-4-isopropylphenol, is extremely unstable[200], and cannot be detected by EPR. On the other hand, π-allylpalladium-containing phenoxy-radicals proved to be fairly stable over a wide temperature range (between −50° and +50 °C). Thus coordination to the transition metal atom led to a significant stabilisation of the unstable free radical. The nature and mode of metal–ligand bonding determine to a significant extent the stability of organometallic free radicals.

The observed sequence of the influences

$$\sigma > \pi \gg n,\ \sigma \rangle\rangle n$$

characterises the ability of the metal atom in complexes of the above type to influence the degree of delocalisation of the unpaired electron in the molecule. In σ-phenyl compounds the unpaired electron is in essence delocalised over the entire molecule (the phenoxy-radical, the metal atom, and the phosphine ligands), which is the reason for the exceptionally high stability of the radicals formed.

Derivatives of sterically hindered phenols can function as π-ligands:



However, in this case the complexes are constructed differently and are diamagnetic derivatives of the phenoxide anion[201].

* * *

The data considered in the present review permit the conclusion that the presence of the unpaired electron in transition metal complexes permits the derivation of information about the detailed characteristics of the structures of complex and organometallic compounds as a result of the application of the EPR method in combination with other physicochemical procedures. The nature of the delocalisation of the unpaired electron in the paramagnetic coordination and organic compounds of transition metals makes it possible to infer the nature of the metal–ligand bonding and the distribution of electron density via the metal–ligand–other ligands bond system. The greatest amount of information can be deduced in the case of complexes with paramagnetic ligands under the conditions of the maximum delocalisation of the spin density of the unpaired electron over the entire molecule. Intramolecular electron transfer then takes place and the systems formed can serve as convenient models for the study of the mechanisms of the oxidation-reduction processes occurring in a living organism.

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