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Coordination Compounds of Transition Metals in the Chemistry of Aromatic Nitro-compounds

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The catalytic possibilities of coordination compounds of transition metals in the chemistry of aromatic nitro-compounds are discussed. The catalytic (including enzymic) reduction of aromatic nitro-compounds by various reductants, namely molecular hydrogen, alkali metal tetrahydroborates, CO + H_2O and CO + H_2 mixtures, alcohols, secondary amines, etc., is considered. The interaction of aromatic nitro-compounds with transition metal complexes, leading either to complexes containing the aromatic nitro-compound or to reduction products, is discussed. The structures of these complexes are classified. The bibliography includes 236 references.

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I. INTRODUCTION

The chemistry of aromatic nitro-compounds is one of the traditional branches of organic chemistry in which considerable theoretical and practical advances have been achieved. Methods and technological processes, based on aromatic nitro-compounds, for the preparation of dyes, explosives, and medicinal preparations have been devised, considerable numbers of molecular complexes have been obtained, etc. At the present time an increased interest in compounds of this class has arisen. A characteristic feature in this instance is the invocation of ideas taken from coordination chemistry: the synthesis of new transition metal complexes incorporating aromatic compounds, the use of coordination compounds as catalysts in the reactions of aromatic nitro-compounds, etc. In this connection, it is useful to discuss new aspects arising in the interrelations between the chemistry of aromatic nitro-compounds and coordination chemistry.

Analysis of the literature has shown that the field of metal complex catalysis has been most fully investigated in relation to catalytic reactions such as the carbonylation and reduction of unsaturated hydrocarbons, deuterium–hydrogen exchange, and free-radical chain oxidation of aromatic compounds. The data on the interaction of aromatic nitro-compounds with transition metal complexes are scattered and have not been surveyed and there is no information about the reaction mechanism. Two recent reviews,[1,2] have been devoted to the reductive amination of aromatic nitro-compounds and their carbonylation with carbon monoxide,[1,2] data on their catalytic hydrogenation can be found in Refs.3–9, and those on their reduction by alkali metal tetrahydroborates have been published by Okushi.[10]

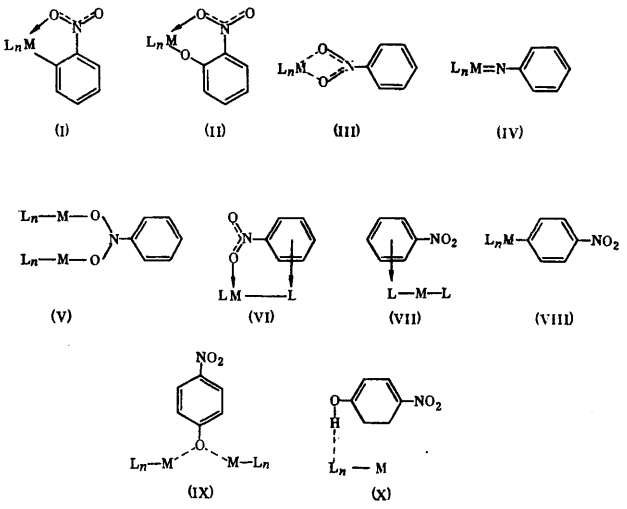
This review discusses the reactions of aromatic nitro-compounds with coordination compounds of transition metals and also the catalytic reduction of aromatic nitro-compounds by various reductants.

II. INTERACTION OF AROMATIC NITRO-COMPOUNDS WITH TRANSITION METAL COMPLEXES

The interaction of aromatic nitro-compounds with non-transition metal complexes (Al, Ga, Hg, etc.) leading to the formation of molecular complexes has long been known and has been investigated in fair detail.[11,18] In the main, the coordination of the metal to the oxygen (one or two atoms) of the nitro-group is postulated.

During the last several years, there has been an appreciable growth of interest in the reactions of aromatic nitro-compounds with transition metal complexes in connection with the elucidation of the mechanism of their catalytic action. Depending on the complex-forming ion, the ligand, and the reaction conditions, the interaction of aromatic nitro-compounds with transition metal complexes leads to the formation of either new stable complexes containing the aromatic nitro-compound (or its reaction product) in the coordination sphere or to organometallic compounds (metallation reaction).

Complexes in which the aromatic nitro-compound is coordinated in a wide variety of ways have been synthesised and to a large extent characterised. The types of compounds are presented below:



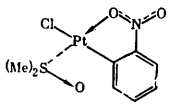
The structures indicated can be subdivided conventionally into two groups—in the first of these the nitro-group is linked to the metal and in the second the nitro-group does not participate in coordination of the aromatic nitro-compound to the metal. We shall not consider the interaction of coordination compounds with aromatic nitro-compounds where the nitro-group is fairly remote from the chelating or strongly accepting centres in the molecule and for this

reason does not participate in complex formation (see, for example, Refs.19–22).

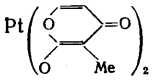
Complexes of type (I) have been formed via the reaction

$$PtCl_2(DMSO)_2 + RC_6H_4NO_2 \xrightarrow{\Delta} PtCl(DMSO)(RC_6H_3NO_2) + HCl + (DMSO).$$
$$R = H, p\text{-Me}, p\text{-Cl}.$$

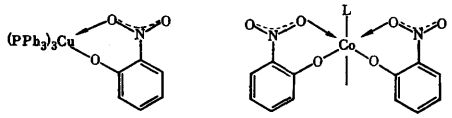
and isolated. The platinum atom has the planar coordination typical of platinum(II) and forms a five-membered ring with a molecule of the nitro-compound in which one of the oxygen atoms of the nitro-group and the carbon atom in the *ortho*-position to the nitro-group coordinate to platinum; the Pt–O and Pt–C bond lengths are 1.96 and 2.06 Å respectively:[23,24]



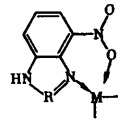
It has been shown by Raman spectroscopy that the nitro-group is coordinated to platinum in nitrobenzene solutions of the complexes[25] $PtCl_2(DMSO)_2$, K_2PtCl_4, and



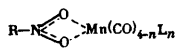
Complexes of type (II) have been isolated for copper, cobalt, and palladium.[26–29] A six-membered metallocycle is characteristic of these compounds, the metal atom are being linked to the oxygen atoms of the nitro- and hydroxy-groups:



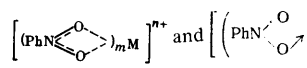
The nickel(II), copper(II), zinc(II), cadmium(II), and mercury(II) complexes of 4(7)-nitrobenzimidazole, investigated by IR, EPR, and electron spectroscopic methods, can be assigned to the same type.[30] It has been shown that these ligands are bidentate; the metal ions are coordinated to the oxygen of the nitro-group and the nitrogen of the imidazole ring with formation of a six-membered metallocycle:



The photolytic or thermal reaction of the pentacarbonylmanganese radicals with aromatic nitro-compounds in the presence of PBu_3 have been investigated by EPR.[31] A cyclic structure in which the manganese atom constitutes a bridge between two oxygen atoms of the nitro-group [type (III)] has been proposed on the basis of the EPR spectra of the stable paramagnetic species:

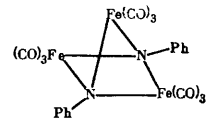


where R = t-butyl, isopropyl, phenyl, 3,5-dichlorophenyl, 2-thienyl, or 3-thienyl. The reactions of transition metal [Fe(III),[32] Co(II), Ni(II), Cu(II), Pd(II), and Mn(II)] chlorides[33] with $SbCl_5$ and aromatic nitro-compounds in an aprotic solvent (CCl_4) lead to the formation of complexes. $Fe(PhNO_2)_6(SbCl_6)_3$, $Fe(PhNO_2)_3(SbCl_6)_3$, and $FeCl(PhNO_2)_2(SbCl_6)_2$ are formed from the iron salt, complexes having the composition $M(PhNO_2)_2(SbCl_6)_2$ are produced from the cobalt, nickel, copper, and palladium salts, and the complex $Mn(Ph.NO_2)_3(SbCl_6)_2$ is formed from the manganese salt. The following structures have been assigned on the basis of spectroscopic studies:



The formation of nitrene derivatives [type (IV)] has been observed in many studies for the Co, Fe, Ru, Pd, Ti, V, Cr, Mo, and W complexes. A crystalline green product, to which the composition $Pd(acac)H(C_6H_5N=)Py$ was assigned on the basis of thermal and spectroscopic analyses, has been isolated.[34] The authors postulate the coordination of palladium to the nitrogen of the nitro-group with formation of a phenylnitrene complex.

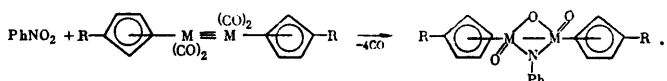
The interaction of nitrobenzene with $Fe_3(CO)_{12}$ in benzene containing methanol [35] or in a mixture of benzene, aqueous alkali, and a phase transfer catalyst,[36] leading to the reduction of nitrobenzene to aniline, has been investigated. A mechanism of the reduction process, involving the formation of intermediate nitrene complexes of iron, has been proposed. The compound



has been isolated and characterised. The authors suggest that the active species is the anion $HFe_3(CO)_{11}^-$. It has been shown that the IR spectra resembling those of the complex described above are observed when nitrobenzene (nitromethane [37]) is added in an He or H_2 atmosphere to the anion $HFe_3(CO)_{11}^-$ on an ion-exchange resin.[38] A similar mechanism has been put forward also for the reaction of nitrobenzene in tetrahydrofuran (THF) with titanium, molybdenum, and iron clusters having the composition $M_xC_4H_8$ ($x \geqslant 2$).[39]

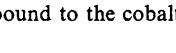
The study of the EPR spectra of the products of the interaction of $[Co(CN)_5]^{3-}$ and [(bis-salicylidene-ethylenediaminato)Co^{2+}] (salen) with an aromatic nitro-compound[40–43] demonstrated the presence of a cobalt nitroxide free radical or radical-anion in which there is a cobalt–nitrogen bond.

In order to investigate the mechanisms of the hydrogenation of aromatic nitro-compounds in the presence of ruthenium complexes, the products of the interaction of nitro-compounds with the complexes in the absence of hydrogen were isolated. Nitrene derivatives, whose structures have been shown to be $Ru_3(CO)_{10}NPh$ and $Ru_3(CO)_9(NPh)_2$ are isolated in an atmosphere of nitrogen after the reaction of nitrobenzene with $Ru_3(CO)_{12}$.[44,45] The same complexes can also be obtained by the reaction of aniline or phenyl isocyanate with ruthenium carbonyl. A reaction has been described in which the complex is fully decarbonylated:[46]



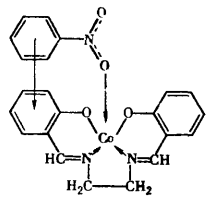
The yield is 40–46%. Hydrogenation of the reaction product under phase transfer conditions leads to the formation of an aromatic amine in a quantitative yield.

The formation of a dimeric compound on interaction of nitrobenzene with cobaloxime has been suggested,[47] the authors assuming that the nitro-group is bound to the cobalt atom via both oxygen atoms [type (V)]:



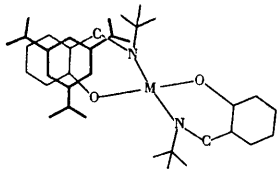
Thus stable complexes are obtained when both oxygen atoms of the nitro-group are coordinated to the metal atom. When the nitro-group is coordinated via one oxygen atom, the complexes are stabilised via the formation of a metallocycle incorporating a ring carbon atom in the *ortho*-position relative to the nitro-group or the oxygen atom of the hydroxy-group. Nitrene complexes with a metal–nitrogen bond are stable.

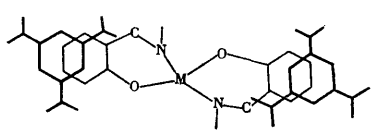
The interaction of aromatic nitro-compounds with cobalt and copper complexes (in which Schiff bases are ligands) has been investigated.[48] It has been shown that the reaction product is characterised by a high-intensity band in the electronic spectra in the range 420–432 nm. A black adduct of Co^{2+}(salen) with nitrobenzene, in which the aromatic ring of nitrobenzene is located above the plane of the ligand and in which the oxygen atom of the nitro-group is linked to the metal [type (VI)], has been isolated:



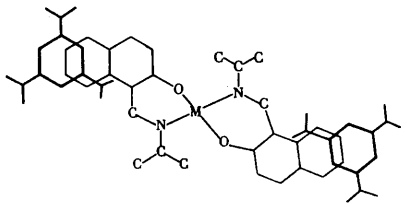
In the complex bis(*N*-*p*-nitrophenylsalicylaldiminato)Cu(II).dioxan, the copper atom is coordinated via four atoms (two oxygen atoms and two nitrogen atoms) of the ligands as a chelate and two monomeric complexes, linked via the centre of symmetry, give rise to a dimer as a result of the formation of a strong axial Cu...O bond. The coordination of the copper atom is built up to a distorted octahedral form via the oxygen atom of the nitro-group, which leads to the formation of an infinite polymer chain.[49]

Many complexes containing highly conjugated ligands—porphyrins, dyes, *o*-hydroxyquinones, and 8-hydroxyquinolines—form donor–acceptor complexes with aromatic nitro-compounds, in which there is no metal–nitro-group bond [type (VII)] ("peripheral mechanism"). The interaction of tetra-*p*-tolylporphyrinatocobalt(II),[50,51] palladium(II), cobalt(II), copper(II), and nickel(II) 5,10,15,20-tetraphenylporphyrinates[52–54] and the dimethyl esters of the meso-porphyrin complexes of cobalt(II) and nickel(II) [55] with 1,3,5-trinitrobenzene and 2,4,7-trinitrofluorenone has been investigated and it has been shown that, under these conditions, the $\pi-\pi$ interaction takes place exclusively on the periphery of the porphyrin and does not involve the metal. X-Ray diffraction studies have demonstrated that *sym*-trinitrobenzene forms 1:1 [56] and 1:2 [57] compounds with M^{2+} complexes of bis-salicylidene-ethylenediamine (salen) and is located exclusively over the π-system of the ligand, the planes of the two ligands being parallel. A similar interaction has been described[58–64] for copper(II) and palladium(II) 8-hydroxyquinolinates with a series of strong acceptors: *sym*-trinitrobenzene, chloranil, etc. In the donor–acceptor complexes formed, the acceptor is localised exclusively over the donor and is not linked to the metal atom:

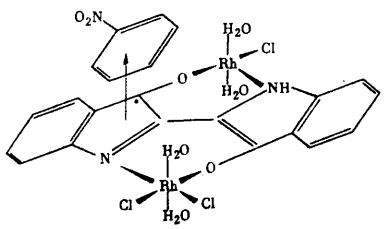




Molecular complexes of 1,3,5-trinitrobenzene with copper(II), nickel(II), and palladium(II) 1-alkylaminomethyl-2-naphthoxides have been synthesised.[65] The structure of the adduct of palladium(II) 1-isopropylaminomethyl-2-naphthoxide with trinitrobenzene has been investigated by X-ray diffraction. The plane of the nitro-compound is parallel to that of the naphthalene ring and trinitrobenzene is disposed over the terminal naphthalene ring:



The interaction of nitrobenzene, a week acceptor, with coordination compounds of transition metals has been studied in a number of investigations. It has been shown that nitrobenzene reacts with haematoporphyrin to form a weak 1:1 complex.[66] Stoichiometric reduction of nitrobenzene by the rhodium(II)–potassium indigo-sulphonate complex in solution[67] proceeds at the expense of the electrons of both the ligand and rhodium(II). A signal whose intensity corresponds to 2–3% of paramagnetic species relative to the amount of the complex has been detected in the EPR spectrum on interaction of nitrobenzene with this complex bound to alumina. The mechanism of the activation of nitrobenzene involves the intermediate formation of a peripheral complex via the π orbitals of the ligand and nitrobenzene:



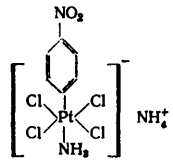
The formation of molecular complexes between nitrobenzene and copper(II) bisalizarinate has been demonstrated by ^{1}H NMR.[68] The nitro-group in the molecular complex is oriented towards the side opposite to that of the copper(II) ion. It has been demonstrated by electronic emission spectroscopy[69] that the character of the interaction of alizarin and palladium bisalizarinate with an aromatic nitro-compound is isotypical which led the authors to the conclusion that the interaction of the nitro-compound with a palladium complex has a peripheral mechanism.

In the 1:1 donor–acceptor complex of the tricarbonylchromanisole and *sym*-trinitrobenzene,[70] there is interaction between the aromatic systems of the nitro-compound and the complex. The planes of anisole and trinitrobenzene form a small angle of 3° and the centres of the planes are somewhat displaced relative to one another, so that the interaction in this system is weaker than between the aromatic systems without the metal.

A specific "metal ion–nitrobenzene" interaction via the hydrogen bond of the NH protons has been observed in a study of the electrical conductivity of [Co(acac)$_2$diamine]X in nitrobenzene.[7,72] Furthermore, there is $\pi-\pi$ interaction in this system between the bipyridyl ligand and the nitrobenzene molecule.

As can be seen from the data presented, a strong $\pi-\pi$ interaction between the aromatic system of the nitro-compound and the highly conjugated ligand is characteristic of complexes of this group [types (VI) and (VII)], the nitro-group either not being involved in complex formation or being additionally coordinated to the metal ion via the oxygen atom.

Complexes of type (VIII) have been isolated after the reaction of nitrobenzene or *p*-nitrotoluene with H_2PtCl_6 in $CF_3COOH-H_2O$. The isomers of the *m*- and *p*-σ-aryl complexes of platinum(IV) were obtained in which the nitro-group does not enter the coordination sphere of platinum:[73]



Nitrophenol can serve as a bridge between two copper atoms [type (IX)], the authors indicating that the IR spectra of structures of type (II) and (IX) do not differ.[27] In the 1 : 1 adduct of *p*-nitrophenol and Cu^{2+}(salen), nitrophenol is disposed between the molecules of the chelate.[74] The oxygen atom of the phenol forms a hydrogen bond with the oxygen of the donor and this adduct is linked solely to the ligand and not to the metal atom. The nitro-group does not participate in the binding to the chelate [type (X)]. A polymeric nitrobenzene complex of nickel stable in air has been isolated:[75]

$$NiO_2(t\text{-BuNC})_2 + PhNO_2 + t\text{-BuNC} \rightarrow Ni(PhNO_2)(t\text{-BuNC})_2.$$

Table 1. Interaction of aromatic nitro-compounds with transition metal complexes.

No.	Aromatic nitro-compound	Metal ion	Type of compound	Method of investigation*	Refs.
1	Nitrobenzene, *p*-nitrotoluene, *p*-chloronitrobenzene	Pt(II)	(I)	RRS, XRD	[23—25]
2	*o*-Nitrophenol, Nitrobenzimidazole	Cu(II), Co(II), Pd(II), Ni(II)	(II)	IR, EPR, XRD	[26—30]
3	Nitrobenzene, 3,5-dichloronitrobenzene, α-nitronaphthalene	Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Pd(II)	(III)	IR, EPR	[31—33]
4	Nitrobenzene	Co(II), Fe(III), Ru(II), Pd(II), Mo(II), Cr, Fe	(IV)	XRD, IR, EPR	[34—46]
5	Nitrobenzene	Co(II)	(V)	IR	[47]
6	Nitrobenzene	Co(II), Cu(II)	(VI)	IR	[48, 49]
7	1,3,5-Trinitrobenzene, 2,4,7-trinitrofluorenone	Co(II), Pd(II), Cu(II), Ni(II), Cr(III)	(VII)	^{1}H NMR, XRD	[50—65, 70]
8	Nitrobenzene	Rh(II), Cu(II), Pd(II), Co(II)	(VII)	EPR, ^{1}H NMR, EES	[66—69, 71, 72]
9	Nitrobenzene, *p*-nitrotoluene	Pt(IV)	(VIII)	XRD, ^{1}NMR	[73]
10	*o*-Nitrophenol	Cu(II)	(IX)	IR, XRD	[27]
11	*p*-Nitrophenol	Cu(II)	(X)	XRD	[74]

*RRS = resonance Raman spectroscopy, XRD = X-ray diffraction analysis, and EES = electronic emission spectroscopy.

The complex $Ni(PhNO_2)_2(PPh_3)_2$ has been obtained in the form of crystals.

Table 1 compiles data on the formation of complexes by aromatic nitro-compounds with transition metal complexes.

III. REDUCTION OF AROMATIC NITRO-COMPOUNDS

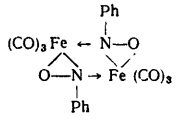
1. Reduction by Transition Metal complexes

Numerous studies have been devoted to the reduction of aromatic nitro-compounds by metal complexes. The iron carbonyl cluster $Fe_3(CO)_{12}$ possesses reducing properties in benzene, hexane, and THF. In methanol-containing benzene, mixing of an equimolar amount of nitrobenzene and $Fe_3(CO)_{12}$ leads to the formation of an aniline.[35] The rate of reaction can be increased by an order of magnitude by introducing a phase transfer catalyst.[36] In a CO atmosphere, an aniline is also the reaction product.[66] The use of this cluster on alumina lowers the selectivity of the reaction; a mixture of an aniline and azobenzene is obtained, the yield of anilines depending on the substituent in the aromatic ring and varying in the range 40—79%, while the yield of azobenzene does not exceed 4—7%.[77] The reducing species is the $HFe_3(CO)_{11}^-$ anion,[78] which can be obtained in its turn by treating $Fe_3(CO)_{12}$ in THF with 1 M tetrabutylammonium fluoride solution. If this reaction is carried out in the presence of *p*-nitrotoluene, *p*-toluidine is detected. Furthermore, this anion can be isolated from the reaction

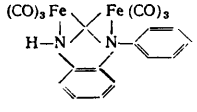
$$Fe_3(CO)_{12} + KF + 18\text{-crown-}6 \rightarrow [HFe_3(CO)_{11}]^-.$$

When manganese pentacarbonyl was treated with $(C_4H_9)_4NF$ or $(C_4H_9)_4NF.3H_2O$, its anion was obtained. It reduces nitrotoluene and nitroanisole to the corresponding anilines in the presence of water in 52—88% yield. The corresponding cobalt compound does not reduce the aromatic nitro-compounds.

Iron pentacarbonyl, in the presence of which aromatic nitro-compounds are reduced to nitroso-compounds, is extremely reactive. The nitroso-compounds subsequently form a complex with the iron. Thus a nitrosoiron complex was isolated from a mixture of 3-chloro-2-methylnitrobenzene with $Fe(CO)_5$ and its structure was determined:[79]



Monomeric or dimeric iron complexes are formed in the reduction of iron pentacarbonyl under the influence of light or ^{60}Co γ-radiation.[80] It has been stated that under other conditions one mole of nitrobenzene can be reduced by one mole of iron pentacarbonyl to azoxybenzene and 1.4 mole is reduced to azobenzene in yields up to 76%. Treatment of nitrobenzene with a large excess of iron pentacarbonyl in hot butanol or with 1.4 mole of iron nonacarbonyl can yield the complex



The reaction of $KHFe(CO)_4$ with nitrobenzene at room temperature takes place exothermically, CO_2 is evolved, and the reaction product is aniline.[81] If bromomagnesioalkyl- or bromomagnesioarylamides are added to the reaction mixture, the reaction products are asymmetric *NN'*-disubstituted ureas (yield 42—99%):[82]

$$R'NHMgBr + Fe(CO)_5 + R^2NO_2 \rightarrow R'NHCONHR^2.$$

It has been suggested that carbamoyltetracarbonylferrate is formed initially and then reacts further with the aromatic nitro-compound.[83]

The interaction of acyltetracarbonylferrates with nitrobenzene[83] leads to anilines. Ferrates are both reducing and acylating agents:

$$R'COFe(CO)_4^- + PhNO_2 \rightarrow R'CONHPh\ .$$

The yield of the target products is 68–86% and the amine R′NHPh is a side product.

The mechanism of the oxidation of the iron-porphyrins by an aromatic nitro-compound has been studied:[84,85]

$$6Fe^{II} + PhNO_2 + 6H^+ \rightarrow 6Fe^{III} + PhNH_2 + 2H_2O\ .$$

The rate of reaction diminishes in the sequence trinitro > dinitro > mononitro. Aromatic nitro-compounds are then reduced to amines, whose yield falls appreciably when various substituents are introduced into the aromatic ring. Comparison of iron-porphyrins with haemoproteins showed that the latter exhibit a very low activity. This effect is associated, according to the authors, with the fact that the rate-limiting stage is the dissociation of the protonated aromatic nitro-compound (by analogy with the mechanism of the oxidation of iron-porphyrins by molecular oxygen[86]). The aromatic nitro-compound interacts directly with the iron atom, although in the presence of a solvent such as pyridine one cannot rule out the possibility of a peripheral mechanism.

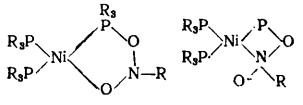
The reaction of *o*-nitrophenol with $[Ru(CO)_3(PPh_3)_2]$ (which is a catalyst of the hydrogenation of aromatic nitro-compounds[107]) takes place in an interesting manner. A ruthenium complex has been isolated[87] in which one nitrophenol molecule is bound to ruthenium via the oxygen atom of the OH group while the other has been transformed into a nitroso-derivative and has been coordinated to ruthenium via the nitrogen of the nitroso-group and the oxygen of the OH group. The nitro-group is not coordinated to ruthenium and is not coplanar with the benzene ring. Complexes of zerovalent nickel also reduce aromatic nitro-compounds to the nitroso-derivatives;[88] the reaction takes place rapidly in benzene with a sharp change in colour:

$$PhNO_2 + Ni(PPh_3)_4 \rightarrow (PhNO)Ni(PPh_3)_2 + OPPh_3 + PPh_3\ .$$

In the presence of nickel complexes, oxygen is transferred from the aromatic nitro-compound to the phosphine in accordance with the following scheme:

$$NiL_4 \rightleftharpoons NiL_3 + L\ ,$$
$$NiL_3 + RNO_2 \rightarrow [Ni^{I}L_3 \cdot RNO_2^-]\ ,$$
$$[Ni^{I}L_3 \cdot RNO_2^-] \rightarrow L_2Ni(ONR) + LO\ .$$

The formation of intermediate complexes with nitrobenzene is then postulated:



When 3,4-dichloronitrobenzene is added to a solution of the $NaBH_4$-treated iridium(IV) complex of chloranilic acid, the 3,4-dichloronitrobenzene radical-anion is formed.[89]

Metal-chelated flavins reduce the aromatic nitro-compound, the reducing property depending on the metal ion and increasing in the sequence Mn(II) < Zn(II) < Ni(II) < Co(II).[90]

Table 2 presents data on the reduction of aromatic nitro-compounds by transition metal complexes.

In conclusion we may note general characteristics. Aromatic nitro-compounds are reduced via the formation of the nitro-compound radical-anion with subsequent reduction to the nitroso-compound. Depending on the complex-forming metal, the nitroso-compound can subsequently give rise to a stable complex with the metal (iron, nickel, cobalt, ruthenium) or it can be reduced with formation of various products (iron).

2. Reduction by Molecular Hydrogen

It is known that the reduction of aromatic nitro-compounds can lead to a series of products:

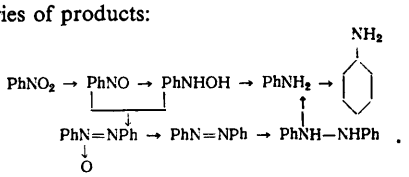


Table 2. Reduction of aromatic nitro-compounds by metal complexes.

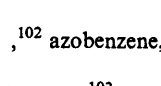
No.	Complex	Aromatic nitro-compound	Reaction products	Remarks	Refs.
1	$Fe_3(CO)_{12}$	Nitrobenzene	Aniline	—	[35,36, 76]
2	$Fe_3(CO)_{12}$	Substituted nitrobenzenes	Substituted anilines, azobenzenes	Complex on Al_2O_3	[77]
3	$Fe_3(CO)_{12}$	*p*-Nitrotoluene	*p*-Toluidine	Addition of tetra-butylammonium fluoride or KF + crown-ether	[78]
4	$Mn_2(CO)_{16}$	ditto	ditto	Ditto	[78]
5	$Fe(CO)_5$	3-Chloro-2-methyl-nitrobenzene	Nitrosoiron complex	—	[79]
6	$Fe(CO)_5$	Substituted nitrobenzenes	Ditto	Under the influence of light or ^{60}Co γ-rays	[80]
7	$Fe(CO)_5$	Substituted nitrobenzenes	*NN*′-disubstituted ureas	Addition of RNHMgBr	[82]
8	$Fe(CO)_4(RCO)$	Nitrobenzene	Amide, amine	—	[83]
9	Iron-porphyrins	Mono-, di-, and tri-nitrobenzenes	Anilines	—	[84, 85]
10	$Ru(CO)_3(PPh_3)_2$	*o*-Nitrophenol	Nitronitroso-ruthenium complex	—	[87]
11	$Ni(PPh_3)_4$	Substituted aromatic nitro-compounds	Nitroso-compounds of nickel	—	[88]
12	Ir(CAA)* + $NaBH_4$	3,4-Dichloro-nitrobenzene	3,4-Dichloronitro-benzene radical-anion	—	[89]
13	Flavin radicals containing manganese, nickel, and cobalt	Substituted aromatic nitro-compounds	Radical-anions of aromatic nitro-compounds	—	[90]

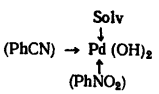
*CAA = chloranilic acid.

The study by Ogata and Sugiyama[91] may be regarded as the first of this kind, but vigorous research has been prosecuted mainly during the last 20 years. One of the first catalysts used in this reaction is cobalt pentacyanide. In aqueous[92] and aqueous alkaline[93,94] solutions close to room temperature, the product of the halogenation of nitrobenzene is azobenzene,[92] while the halogenation of nitrobenzen and *o*-nitroanisole results in a mixture of azo- and hydrazo-compounds,[93] while at elevated H_2 pressures a mixture of an amine and an azo-compound is produced.[94] Complexes of bisdimethylglyoximatocobalt(II) catalyse the hydrogenation of aromatic nitro-com pounds under mild conditions to an aniline and hydrazobenzene an the hydrogenation of methyl *p*-nitrocinnamate to methyl *p*-amino-cinnamate in 78% yield.[95] When nitrobenzene is reduced in the presence of cobalt pentacyanide, the rate of reaction depends on th

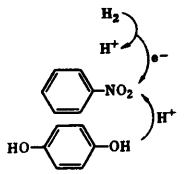
OH^- concentration and the catalyst : substrate ratio; thus, when the ratio of cobalt to nitrobenzene is less than unity, the reaction does not occur. In an aqueous alcoholic medium with added KOH, the reaction products are azo- and azoxy-benzenes.[96]

Cobaloximes having the composition $Co(DMG)_2OAc$ and $[Co(DMG)_2]_2CO_3$, where DMG = dimethylglyoxime, are more active catalysts.[97] The catalytic activity is manifested only in the presence of an amine, for example, morpholine. In a mono-olefin–nitrobenzene mixture, the latter is hydrogenated selectively,[98] while isoprene fully inhibits the reaction. It has been suggested that the hydrogenation proceeds via an intermediate dinuclear complex.[99] The presence of a stronger base (KOH, NaOH) is necessary for the manifestation of catalytic activity by the complex (DMG) $(PPh_3).XCo^I.C_2H_5OH$ (X = Cl or Br).[100] At elevated hydrogen pressures, the reaction takes place also in the absence of a base. In contrast to the previously study, Datta et al.[100] suggest that the hydrogenation takes place via the formation of an intermediate phenylnitrene complex. The copper complex $Cu^IBr(PPh_3)_3$ is active under severe conditions.[101] The nitrobenzene halogenation products are aniline (75–79%), azobenzene (5–10%), and nitrosobenzene (2–7%). It has been shown that in an atmosphere of hydrogen the initial complex is transformed into the hydride complex $[CuHBr(PPh_3)]_2$, while at the end of the reaction the complex $(PhN=NPh)Cu_2(PPh_3)_4Br_2$ was isolated.

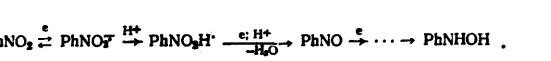
Palladium and platinum complexes are more active and selective. Under mild conditions, nitrobenzene was hydrogenated to aniline (98%) in the presence of the $NaBH_4$-treated complex PdL_2Cl_2 (where , [102] azobenzene, and pyridines[103]). Hydrazobenzene [102] or azobenzene [103] may be present as impurities. A high yield of aniline was obtained also in the presence of the $Pd(PhCN)_2Cl_2$ catalyst.[104] At elevated hydrogen pressure, the yield of aniline falls to 65%.[105] New bands appeared in the electronic and infrared spectra after the addition of nitrobenzene to the complex, which the authors attributed to an intermediate complex having the composition



The mechanism of the reduction of nitrobenzene in an aprotic solvent (DMSO) in the presence of the $PtCl_2(DMSO)_2$ + $NaBH_4$ catalyst and added quinones has been investigated.[106] Under the hydrogenation conditions, the quinones are rapidly and quantitatively reduced to hydroquinones, which facilitates the reduction of nitrobenzene as a result of the protonation of the intermediate reduction products. The function of the catalyst consists in electron transfer from H_2 to nitrobenzene, while the role of the hydroquinone, introduced into the system or formed on hydrogenation of quinone, is to transfer a proton. The formation of donor–acceptor complexes of nitrobenzene with hydroquinone has been postulated:

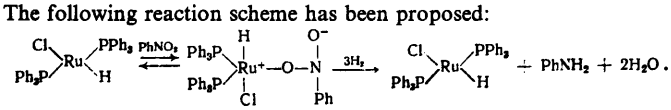


The reduction of nitrobenzene is described by the scheme



The final hydrogenation product is phenylhydroxylamine.

The ability to catalyse the selective reduction of dinitrobenzenes to the corresponding nitroanilines is a unique feature of ruthenium complexes.[107–109] Substituted nitrobenzenes are hydrogenated only at the nitro-group (in the presence of ruthenium and iron complexes). The following reaction scheme has been proposed:



Here one can imagine that the stage involving the interaction with the nitro-compound is more complex (see, for example, Pizzotti and Crotti[87]). The iron complexes are less active. The complex $RuCl_2.(PPh_3)_3$ exhibits the highest specificity in the hydrogenation of dinitrobenzene to nitroanilines,[107,110] which permitted the selective hydrogenation of mixtures of dinitro- and nitro-compounds. For example, in a mixture of nitrobenzene with *p*-dinitrobenzene, only *p*-dinitrobenzene is reduced (to *p*-nitroaniline).[111] *o*-Substituted nitro-compounds are more effectively hydrogenated in the presence of a quaternary ammonium base and ruthenium(II) and ruthenium-(III) complexes;[112] alcohols, halogenohydrocarbons, or ethers can serve as solvents. The selectivity with respect to reaction products is 85% for a 95% conversion.

The dimeric ruthenium hydride, obtained from $RuCl_2.(\eta^6\text{-}C_6Me_6).(PPh_3)$ and Na_2CO_3 in isopropyl alcohol, shows a low catalytic activity in the hydrogenation of nitrobenzene; the yield of aniline reaches 38% after 36 h at 50 °C and 50 atm.[113]

The titanium(III) compounds obtained by reducing the titanium-(IV) compounds $R_nTi^{IV}Cl_{4-n}$ (where R = $MeCOO^-$, PhH_2COO^-, or $\alpha\text{-}C_{10}H_7CH_2COO^-$; n = 0, 1, 2) with molecular hydrogen catalyse the hydrogenation of nitrobenzene to aniline in the presence of heterogeneous catalysts in dimethylformamide (DMF).[11]

Wilkinson's complex $RhCd(PPh_3)_3$ is inert in the hydrogenation of aromatic nitro-compounds. When a phosphine or an amine is added to the reaction medium, nitrobenzene is hydrogenated to aniline at a low rate (0.2–2.6 moles of H_2 per mole of rhodium per minute).[115–117] Under the same conditions, the rhodium complex Rh(hexa-1,5-diene)Cl_2 catalyses the reduction of substituted nitro-compounds, appreciable dehalogenation being observed for halogeno-derivatives.[116] The complex $RhPy_3Cl_2$, which manifests a catalytic activity after treatment with $NaBH_4$ and DMF, has been studied in detail.[115,118,119]. The intermediate catalytically active complex $Py_2.(DMF)RhCl(BH_4)$ was isolated. It was noted that the catalyst decomposes after a time owing to the reduction of the ligand—pyridine. The dinuclear rhodium complexes with a bridging nitrogen heterocycle, namely [(COD)ClRh(μN–N)RhCl(COD)], where COD = cyclo-octa-1,5-diene or *NN'*-bipyridyl, are more stable.[120,121] After treatment with $NaBH_4$, the complexes catalyse the hydrogenation of nitrophenols and nitrobenzoic acid. The authors did not characterise the active species.

The catalytic activity of sulphur-containing rhenium complexes has been investigated in a number of studies. At 95 °C and 1–40 atm H_2, nitrobenzene and *o*-nitrotoluene were hydrogenated to the corresponding anilines in the presence of complexes with thiourea or mercaptobenzimidazole $[ReOL_2X_3].2H_2O$;[122] the rhenium thio-complexes $Re_2S_2L_8$, where L = $CS(NH_2)_2$, Cl^-, or H_2O, catalyse the conversion of nitrobenzene to azoxybenzene in DMF.[123,124]

Metal clusters have been investigated in recent years as catalysts. The palladium cluster $Pd_5(PPh)_2$ in DMF,[125] the complex obtained by the interaction of the platinum cluster $[Pt_3Sn_8Cl_{20}]^{4-}$ with cyclo-octa-1,5-diene and having the composition $(C_6H_{12})_3Pt_3Sn_2Cl_6$,[126] and soluble polynuclear rhenium thio-complexes[124] catalyse the hydrogenation of nitrobenzene under mild condtions. The reaction has been investigated potentiometrically[126] and it has been shown that the platinum is in the zerovalent state. At temperatures in the range 100–130 °C and pressures in the range 100–300 atm, the iron

cluster $[(\eta^5\text{-}C_5H_5)Fe(\eta^3\text{-}CO)]_4$, in which each iron atom is linked to three other iron atoms and three carbonyl ligands, is active; the yield of aniline is 6–31%.[127]

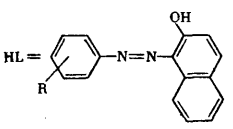
Catalysts obtained by immobilising complexes (mainly palladium and platinum) on carriers have been used successfully. Palladium complexes with polyvinylpyrrolidinone and polyacrylic acid fixed on silica gel,[128] the $Pd(PPh_3)_n^{2+}$ complex on organic and inorganic carriers,[129] the palladium(II) complex on γ-aminopropyl-containing silica gel,[130] and palladium complexes with chloromethylated polystyrene treated with anthranilic acid,[131–133] with a polymeric carrier containing oxime groups,[134,134] with polymeric ligands containing NH groups in the polymer chain,[136–138] etc. have a high activity in the hydrogenation of aromatic nitro-compounds. The main reaction products are the corresponding anilines. Dinitro-compounds can be hydrogenated stepwise with isolation of the mononitro-compounds.[130] It has been noted that the hydrogenation of *p*-chloronitrobenzene is accompanied by dehalogenation.[132] The platinum-nylon catalyst, familiar in the selective hydrogenation of benzene to cyclohexene, hydrogenates nitrobenzene and its derivatives in the liquid phase.[139]

The most active catalysts in the reduction of aromatic nitro-compounds are complexes based on platinum-group metals with highly conjugated ligands (arylazonaphthols, azobenzene, *o*-quinones, *o*-hydroxyquinones, γ-indigoid dyes). The reactivity of the majority of the catalysts which were described is associated with the non-complementary character of the process. The intermediate metal hydride complex is a two-electron reductant, while nitro-compounds are one-electron acceptors.

In complexes incorporating ligands with a branched system of π-bonds, there is a possibility of electron transfer via a peripheral mechanism through the ligand.[5,140] At the beginning of our review, the list of such complexes is given in which donor–acceptor interaction takes place between the aromatic nitro-compounds and the highly conjugated ligand (Table 1). The use of catalysts of this kind made it possible to achieve effective and selective hydrogenation of aromatic nitro-compounds under mild conditions:[141–143]

$$RC_6H_4NO_2 \rightarrow RC_6H_4NHOH\ (96—99\%),$$
$$RC_6H_4NO_2 \rightarrow RC_6H_4NH_2\ (100\%),$$
$$C_6H_4(NO_2)_2 \rightarrow H_2NC_6H_4NO_2\ (95—98\%),$$
$$ClC_6H_4NO_2 \rightarrow ClC_6H_4NH_2\ (99{,}9\%).$$

N-Arylhydroxylamines have been synthesised in 96–99% yield in the presence of the platinum complexes $Pt_2L_3(HL)Cl$, where



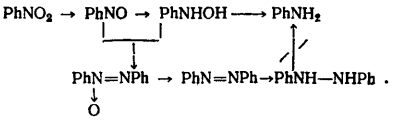
R = H, 4-Me, 2,4-$(Me)_2$, or 4-SO_3Na and L are the corresponding benzeneazonaphthoxides [144–148] or PtQ_2 (where Q = *o*-hydroxyquinones).[149] Platinum complexes with azobenzenes exhibit a lower selectivity (the yield of *N*-phenylhydroxylamine is 55%).[150] The corresponding palladium complexes of azobenzenes[151] are more active then the platinum complexes.[57,150] The reaction takes place via the formation of phenylhydroxylamine, but the final product is aniline. Palladium complexes of *o*-hydroxyquinones[152] and platinum complexes of *o*-γ-pyrone and *o*-quinone[103] are effective catalysts of the hydrogenation of aromatic nitro-compounds to anilines. The reduction of dinitrobenzenes to mononitro-derivatives is catalysed by platinum and palladium complexes of *o*-hydroxyquinones[153,154] and the reduction of halogenonitrobenzenes to the corresponding halogenoanilines (without the occurrence of the dehalogenation side reaction) is catalysed by platinum, rhodium, and iridium complexes.[155–159]

Thus the synthesis and use of complex catalysts containing as ligands large conjugated systems with a considerable electron capacity constitutes an extremely fruitful and promising development.

3. Reduction by Alkali Metal Tetrahydroborates

The reduction of aromatic nitro-compounds by alkali metal tetrahydroborates in water and aqueous alcoholic solution of alkali is known to lead to the $PhNO_2^-$ radical-anion,[160] while the reaction in diglyme at elevated temperatures affords azoxybenzene.[161] Transition metal complexes catalyse the reduction process. The cobalt complexes have been most thoroughly investigated.

The reduction of nitrobenzene by $NaBH_4$ in the presence of cobaloxime $H-Co(DMG-H_2)(PPh_3)$ on heating in 50 alcoholic solution was first observed by Sal'nikova and Khidekel'.[162] Nitrobenzene was reduced quantitatively to a mixture of azobenzene (30%), azoxy-benzene (60%), and aniline (10%). The same mixture was obtained in the presence of the complex $H-Co(DMG-H_2)Py$.[151,163] Nitrobenzene and the products of its incomplete reduction have been reduced[164] with sodium and potassium tetrahydroborates in the presence of cobalt(III) complexes—cobalt bisguanide, the cobalt–salen complex, and the cobalt complex of a macrocyclic Schiff base. The complexes were compared with vitamin B_{12} and its model—the cobalt bisdimethylglyoximate complex. The general characteristic of the systems investigated have been discovered: the Co^{3+} ion is reduced to Co^+ or the cobalt(III) hydride; Co^{2+} interacts weakly and Co^+ and the hydride interact strongly with the substrate. The reaction proceeds mainly in the forward direction: nitrobenzene → nitrosobenzene → phenylhydroxylamine → aniline. Among the side products, azoxy- and azo-benzenes were detected, ar increase in the reaction temperature from 40° to 100 °C resulting in an increase in the yield of aniline. The same features have been observed when hydroxycobalamin was used as the catalyst.[165] It has been suggested that the catalytic system involves the formation of an unstable cobalt–nitrogen intermediate compound (nucleophilic addition to an unsaturated system). On the basis of kinetic measurements, the following reaction mechanism has been put forward:[165]



Cobalt(II) compounds are also active. The first stage is probably the reduction by alkali metal tetrahydroborates of cobalt(II) to cobalt(I), which is in fact the active catalytic species. The composition of the product varies markedly as a function of the nature of the ligand and the solvent. Thus in methanol in the presence of $Co(II)-Co(DMG)_2$, $CoCl_2$, $Co(AcO)_2$, etc., hydrazobenzene and aniline were obtained,[166] in the presence of the Co(II)–mesoporphyrin complex the products were phenylhydroxylamine (34%) and azoxybenzene (35%),[167] while in the presence of the complexes $Co(bipy)_3^+$ and $Co(bipy)_3^{3+}$ the products were phenylhydroxylamine and aniline.[168] The last two cobalt complexes react rapidly with the tetrahydroborate to form a cobalt(I) complex. The nitrile group is reduced faster than the nitro-group, which enabled the authors to carry out the selective reduction of *p*-nitrobenzonitrile to *p*-nitrophenylmethylamine at –10 °C in the presence of the $CoCl_2 + NaBH_4$ system.[169] On raising the temperature, the nitro-group is also reduced.

The highest yield of aniline has been achieved in the presence of the $CuCl_2 + NaBH_4$ catalytic system.[170] In the series of metal acetylacetonates, the highest activity is manifested by copper acetylacetonate,[171] in the presence of which the yield of aniline reaches 90%.

Nickel complexes are active in an inert atmosphere. In water at 70 °C in the presence of cyanonickel complexes,[172] nitrobenzene is readily reduced to azoxybenzene. In an alcoholic medium under the

same conditions in the presence of the $Ni(PPh_3)_2Cl_2$ complex, substituted nitrobenzenes are reduced to the corresponding anilines in 80–88% yield.[173] The reaction selectivity changes sharply when nickel complexes fixed on polymers containing PPh_2 or CH_2PPh_2 groups on the surface are used—the main product is azoxybenzene (up to 85%) with an admixture of azobenzene.[174]

Rhodium(III) complexes, which form hydrides, for example, the hydridochlorotriethylenetetra-aminerhodium(III) cation, catalyse the reduction of nitrobenzene to aniline in solution in aqueous methanol.[175] It is noteworthy that the reduction of aromatic nitro-compounds by alkali metal tetrahydroborates has not found extensive application owing to the low activity and selectivity.

4. Reduction by the Synthesis Gas

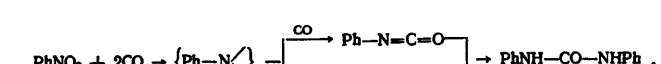
Although the first communication about the reduction of aromatic nitro-compounds by the CO + H_2 mixture in the presence of iron pentacarbonyl appears in 1925,[176] studies in this field were initiated much later. Virtually all the investigations demonstrated that catalytic activity is manifested by transition metal carbanions. The complexes $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ [177,178] in benzene or a benzene–alcohol mixture at 120 °C and 100 atm CO + H_2 catalyse the reduction of nitro-compounds to amines in 94–100% yield:

$$PhNO_2 + 2CO + H_2 \rightarrow PhNH_2 + 2CO_2 .$$

Diphenylurea is a side product (5–6%).

In the presence of cobalt carbonyl, *p*-nitrobenzyl alcohol is reduced to a polymer of *p*-aminebenzyl alcohol (44%), while nitrobenzene is reduced to acetanilide (44%).[179] These results can be explained by the presence of acetic acid (obtained as a result of hydrolysis on synthesis of cobalt carbonyl from cobalt acetate); aniline has not been detected. The reduction of nitrobenzene, *m*-dinitrobenzene, and 2,4-dinitrotoluene under hydroformylation conditions is catalysed by rhodium, iridium, iron, and osmium carbonyls. Iron carbonyl is the least active, while osmium carbonyl is active even in the absence of hydrogen.[180] The yield of the amino-product is 97%. The low activity of iron pentacarbonyl has also been indicated by L'Esplattenier et al.[181]

Ruthenium(III) complexes, namely ruthenium dodecacarbonyl, ruthenium pentacarbonyl, and trisacetylacetonatoruthenium, are active catalysts. Urea was detected among the products for the $C:H_2 > 1$ ratio, its amount increasing with increase in the quantity of CO in the mixture. It has been suggested that a phenylnitrene complex is an intermediate:[181]

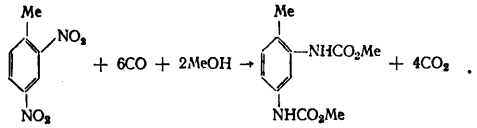


The introduction of sodium methoxide into the reaction medium alters the course of the reaction:

$$PhNO_2 + CO + H_2 + NaOMe \xrightarrow{M_x(CO)_y} PhNHCOH + PhNHCOOMe + PhNH_2 + PhNHCONHPh + PhN{=}NPh .$$

where M = Fe or Ru; the main products in the presence of ruthenium carbonyl are PhNHCOH and $PhNH_2$, while the products in the presence of iron cargonyl are PhNHCOOMe and PhNHCO. .NHPh.

The reduction of an aromatic nitro-compound in the presence of carbon monoxide and alcohol is of greater interest; carbamates, usually synthesised via a multistage process, are then obtained.[182] The ruthenium complexes $Ru_3(CO)_{12}$ and $Ru(CO)_3(PPh_3)_2$ are effective catalyst in the presence of tetraethylammonium chloride as the cocatalyst.[183] A monocarbamate has been obtained in 93% yield from the mononitro-compound, while the dinitro-compound gave rise to the dicarbamate in 50% yield:



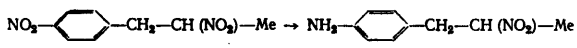
In the absence of the tetra-alkylammonium salt, the main product is aniline. The corresponding iron compounds are inactive. It has been suggested that the reaction proceeds via the formation of a nitrene derivative of ruthenium, i.e. $Ru_3(CO)_{10}NPh$. The same features have been observed when the reaction is carried out in the presence of the platinum complex $PtCl_2(PPh_3)_2$;[184] the reaction is promoted by Lewis acid.

5. Reduction by the CO + H_2O Mixture

The possibility of reducing nitro-compounds to the corresponding amines by the CO + H_2O mixture has been studied vigorously during the last ten years. Rhodium complexes are widely used. Rhodium carbonyl complexes $Rb_6(CO)_{16}$ and $[Rh(CO)_2Cl]_2$ catalyse the reduction of nitrobenzene at 150 °C and CO pressure of 50–120 atm; the yield of aniline reaches 85–95% and the formation of urea or formamide derivatives is not observed:[185]

$$PhNO_2 + 3CO + H_2O \rightarrow PhNH_2 + 3CO_2 .$$

Iron carbonyls are also active. The first stage is probably the formation of a nitrene derivative. If the reaction is carried out in pyridine[185] but in the presence of added *NN*-dimethylbenzylamine,[186] the selectivity is significantly higher. The attempt to heterogenise the catalyst by grafting it to the Amberlist A-2 resin modified with *NN*-dimethylbenzylamine was unsuccessful: the rate of hydrogenation fell and the senstivity of the catalyst to air increased. Aliphatic nitro-compounds are not reduced in this system, which made it possible to carry out a selective reduction:



The study of the role of amines[187] led to the conclusion that the acceleration of the reaction may be a consequence of the formation of a more active species incorporating the amine as a ligand. The $Rh_6(CO)_{16}$–γ-aminopyridine system, which makes it possible to reduce nitrobenzene under mild conditions (80 °C, CO pressure below 1 atm), is optimal. Other rhodium clusters are also active—$Rh_2(CO)_4Cl_2$ and $Rh_4(CO)_{12}$; the iron and ruthenium clusters exhibit a low activity. It has been noted that the rate of reaction can be increased significantly in the presence of the $Rh_3(CO)_{12}$ and $Ru_3(CO)_{12}$ clusters only by introducing chelating nitrogen-containing bases into the reaction mixture.[188] Thus the yield of aniline reaches 100% after the introduction of 3,4,7,8-tetramethylphenanthroline or 3,4,5,6,7,8-hexamethylphenanthroline [189] in the proportions chelating agent : rhodium = 3.

The use of iron carbonyl $Fe(CO)_5$ as the catalyst of the reduction of nitrobenzene leads to the formation of aniline at 25 °C and a CO pressure of 50 atm if the reaction is performed in aqueous glyme with added triethylamine. Part of the catalyst is then irreversibly decomposed with formation of iron oxides.[190] The reaction proceeds rapidly at pH 12. The reducing species is $HFe(CO)_4^-$. $Rh_6(CO)_{16}$, $Os_3(CO)_{12}$, $H_2Os(CO)_{10}$, $H_4Os_4(CO)_{12}$, and $Ir_3(CO)_{12}$ are active under the same conditions. In their study of the reaction mechanism with the aid of CO + D_2O, the authors showed that, at least to the

extent of 88%, the reducing agent is the CO + D_2O mixture and not D_2 (reduction via the reaction CO + $D_2O \rightarrow CO_2 + D_2$), as suggested previously by Iqbal.[191] Furthermore, the rate of generation of deuterium (or hydrogen) is lower by two orders of magnitude than the rate of reduction of nitrobenzene, i.e. the reaction with molecular hydrogen does not play an important role.

At 80 °C and a CO pressure of 60 atm, the platinum complex $PtCl_2(PPh_3)_2$ is active in the presence of the Lewis acids $ZnCl_2$, $SnCl_2$, $SnCl_4$, etc., the highest rate being observed after the introduction of $SnCl_4$.[192] The yield of aniline falls on reducing the temperature or replacing the CO + H_2O mixture by hydrogen. The reaction takes place in stages, the Lewis acid being necessary in the second stage:[193]

$$PhNO_2 + 2CO \rightarrow PhN\langle + 2CO_2 ,$$

$$PhN\langle + CO \rightarrow PhNCO ,$$

$$PhNCO + H_2O \rightarrow [PhNHCOOH] \xrightarrow{-CO_2} PhNH_2 .$$

The dependence of the yield of aniline on the initial CO pressure has been noted for the ionic ruthenium complex $[Ru(COD)Py_4].(BPh_4)_2$. Thus the yield of aniline (in THF) is 36% at 15 atm, 62% at 30 atm, 74% at 45 atm, and 90% at 60 atm.[194] The authors rule out the possibility of the formation of an intermediate phenylnitrene derivative, since *o*-nitrobiphenyl produces only *o*-aminobiphenyl without an admixture of carbazole. The reaction does not occur when water is replaced by methanol or phenol.

The palladium complexes $Pd_3(CO)_3(PPh_3)_4$, $Pd_4(CO)_3(PPh_3)_4$, and $Pd_{10}(CO)_{12}(PPh_3)_6$, which are active and stable in the presence of an excess of triphenylphosphine, have been synthesised.[195]

In conclusion, we shall describe systems in which water may be replaced by unsaturated compounds. In the presence of $Rh_6(CO)_{16}$ the following reactions can be achieved with a high efficiency:[185]

$$2PhNO_2 + H_2 + 5CO \rightarrow PhNH{-}CO{-}NHPh + 4CO_2 \quad (70{-}80\%)$$

$$PhNO_2 + R{-}CH{=}CH_2 + 2CO \rightarrow Ph{-}N\langle_{CH_2{-}CH(R)} + 2CO_2 , \quad (60\%)$$

$$PhNO_2 + Ph{-}C{\equiv}C{-}Ph + 4CO \rightarrow Ph{-}N\langle_{C(=O){-}C(Ph)=C(Ph){-}C(=O)} + 2CO_2 , \quad (85\%)$$

$$PhNO_2 + PhCHO + 3CO \rightarrow PhCH{=}N{-}Ph + 3CO_2 , \quad (60{-}85\%)$$

$$PhNO_2 + C_6H_4(CHO)_2 + 3CO \rightarrow C_6H_4(CH_2)(CO)N{-}Ph + 3CO_2 . \quad (50{-}60\%)$$

6. Reduction by Alcohols

A few studies are known where alcohols were used as reductants for aromatic nitro-compounds. Depending on the alcohol and the catalyst, the reaction products can be aromatic amines, 2,3-dialkylquinolines, hydrazo- and azo-derivatives, and arylhydroxylamines. When an aromatic nitro-compound reacts with an alcohol, hydrogen is transferred catalytically from the alcohol; aniline and an aldehyde (stage I) are then formed and can subsequently give rise to various condensation products (stage II). It has been shown that the ruthenium complex $RuCl_2(PPh_3)_3$ catalyses this reaction and a mixture of products is obtained:[196]

$$PhNO_2 + RCH_2CH_2OH \xrightarrow{180^\circ} PhNH_2 + \text{(2-R-quinoline)} + PhNHCH_2CH_2R + PhN(CH_2CH_2R)_2$$

In methanol and isopropyl alcohol, the reaction proceeds selectively (stage I alone); in ethanol, propanol, and butanol, it is possible to obtain 10–40% of quinolines (stage II). A reaction scheme has been proposed to which a ruthenium chelate complex of a Schiff base dimer is an intermediate.[197] A high yield of mono- and di-alkylquinolines is attained in the presence of equimolar mixtures of rhodium and molybdenum complexes;[198] the latter complex, as a Lewis acid, promotes the condensation reaction.

In the absence of molybdenum compounds, rhodium complexes catalyse only the first stage.[199]

Rhodium complexes containing triphenylphosphine are active in solution in a base. Under these conditions, dinitro-compounds are not reduced.[198] The iridium complexes $Ir^I(X)(CH_2{=}CH_2)_2Cl$, where X = 2,2-bipyridyl or 1,10-phenanthroline and some of its derivatives, is the most active.[200] The activity is satisfactorily correlated with the pK_a of the chelate [chelating agent?]. The reduction reaction proceeds in stages and, by altering the alkali : catalyst ratio, it is possible to obtain a high yield of azo- or hydrazo-derivatives. In the presence of the 4,4-diphenylbipyridyl complex, arylhydroxylamine was isolated in a high yield.

The above procedure is extremely promising, permitting the simultaneous synthesis of products of practical importance (for example, anilines and ketones or aldehydes). Extensive search for more active, stable, and readily available catalysts is essential.

IV. ENZYMIC REACTION OF AROMATIC NITRO-COMPOUNDS

The biological activity of aromatic nitro-compounds, which is manifested by their toxicity[201] (cardiac poisons) and mutagenic,[202] carcinogenic,[203–205] and antibacterial[206–209] activities, is associated with their enzymic reduction. The reduction to aromatic amines or other derivatives is effected by animal tissue homogenates (animals ranging from fish to mammals[210,211]) under aerobic conditions. In animal organisms, aromatic nitro-compounds accumulate mainly in the liver, so that most of the studies have been devoted to the metabolism of aromatic nitro-compounds in mammalian livers.

It has been shown that the reducing activity is localised both in the soluble (cytosol) fraction and in the microsomal fractions, the electron donors being NADP and NADP-H_2 (nicotinamide adenine dinucleotide phosphate and its reduced form). The reduction in cytosol is catalysed by xanthine oxidase[212–214] or DT-diaphorase[215] (enzymes containing an iron–molybdenum cluster linked to sulphur[216,217]). In the microsomal fraction, the reduction of aromatic nitro-compounds is catalysed by other enzymes. *p*-Nitrobenzoic acid can be reduced by purified NADP-H_2-cytochrome *c* reductase, isolated from microsomes, in the presence of flavin adenine dinucleotide.[213,218] Cytochrome P-450 [219–220] or cytochrome b_5 in the presence of NADP-cytochrome b_5 reductase also possess reducing capacity. Later studies established that both microsomal components—NADP-H_2-cytochrome P-450 reductase and cytochrome P-450—are essential for the reduction of nitrobenzene to aniline.[222] The reductase catalyses the first stage in the reduction of the nitro-group, while both components are essential for the reduction of the intermediate arylhydroxylamine. The same features have been observed also in the reduction of *p*-nitrobenzoic acid. The authors note that nitrobenzene-reducing activity is in the main concentrated in the microsomal fraction, while the cytosol fraction exhibits a low activity.

The high activity of an enzyme system comprising three protein components, namely cytochrome b_5, NADP-cytochrome b_5 reductase, and an unknown protein factor, has been noted.[221] The necessity for the presence of several enzymes has also been emphasised in other studies.[223–225] It a study involving microsomal enzymes from

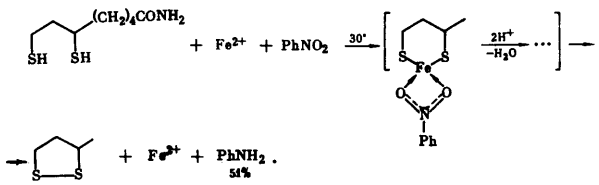
mouse liver homogenate, it has been shown that there are at least two uridine diphosphate transglucuronylases, in the presence of which it is possible to synthesise glucuronide from uridine diphosphate glucuronate and *p*-nitrophenol.[223-225]

The final products of the reduction of aromatic nitro-compounds are usually the corresponding anilines, but it is possible to isolate also intermediate reduction products. It has been shown[203] that the reaction proceeds via the pathway $-NO_2 \rightarrow -NHOH \rightarrow -NH_2$, different enzymes being active in the first and second stages.

The reduction of 2,4-dinitrotoluene (by cytosol xanthine oxidase) to 2,4-diaminotoluene takes place in stages via 2-amino-4-nitrotoluene and 4-amino-2-nitrotoluene.[226,227] Nitroso-derivatives have not been observed, although their formation is entirely probable, since it has been shown that nitrite reductase in micro-organisms and plants reduces nitrite to hyponitrite and further to hydroxylamine and ammonia:

$$NO_2^- \rightarrow N_2O_4^{2-} \rightarrow NH_2OH \rightarrow NH_3 .$$

The enzymes are known to contain iron thiols;[217] studies[228,229] on the reduction of monosubstituted nitrobenzenes in the presence of the dihydrolipoamide (coenzyme in acyl transfer and redox reactions)—iron(II) system in a weakly basic medium are therefore of interest:



It has been noted that the system is unreactive in relation to the reduction of C=C, C=O, CN, and ester groups. The yields of the products (in %) are as follows:

(a) for *p*-substituted aromatic nitro-compounds:

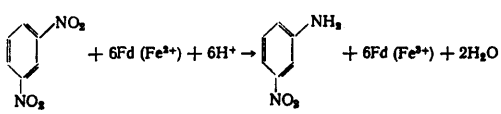
CH_3	OCH_3	NH_2	CN	$COCH_3$	$OCOCH_3$	Cl
35	73	77	94	90	66	58

(b) for *o*-substituted aromatic nitro-compounds:

$COCH_3$	CHO	OCH_3	NH_2	CN
73	67	81	97	84

In the series of thiols, the highest activity is shown by cysteine.

The reduction of 2,4-dinitrophenol, nitrobenzene and *m*-dinitrobenzene by ferredoxin (and iron-containing protein) has been described:[230]

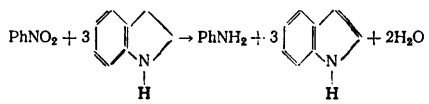


where $Fd(Fe^{2+})$ is the reduced form of ferredoxin, which acts in this reaction as a single electron donor. 2,4-Dinitrophenol is reduced under these conditions to 2-amino-4-nitrophenol.

It is seen from the data presented in this Section that the enzymic reduction of aromatic nitro-compounds takes place in the same way as the reduction by transition metal complexes. An unusual feature is that the enzyme systems are mainly iron and molybdenum clusters linked to sulphur. Comparison of the enzyme systems with coordination compounds shows that the enzyme systems are more selective and that catalytic properties most similar to theirs are shown by platinum group metal complexes with highly conjugated ligands.[4]

V. OTHER REACTIONS

Hydrogen transfer from cyclic amines to aromatic nitro-compounds catalysed by noble metal salts has been described:[231,232]



A high activity has been observed for $RuCl_3.H_2O$ and $RhCl_3.3H_2O$, in the presence of which the yield of aniline is 88 and 82% respectively. Palladium, rhenium, and platinum chlorides are weakly active, while cobalt and nickel compounds and phosphine complexes of rhodium and ruthenium do not catalyst the reaction. Secondary cyclic amines—indoline, tetrahydroquinoline, 3-pyrroline, piperidine, and pyrrolidine—are effective hydrogen donors. The authors explained this by their pronounced coordinating properties. The rate-limiting stage is the activation of the nitro-group, since the intermediate nitrosobenzene and phenylhydroxylamine are reduced under these conditions faster by two orders of magnitude than the nitro-group, while azo- and hydrazo-benzene are reduced an order of magnitude faster. A mechanism involving the coordination of the aromatic nitro-compound to the complex has been suggested:

$$RhCl_3 + Ind \rightarrow Rh^ICl + Inl + 2HCl ,$$
$$Rh^ICl + PhNO_2 \rightarrow Rh^ICl\,(PhNO_2) ,$$
$$Rh^ICl\,(PhNO_2) + 3Ind \rightarrow Rh^ICl + PhNH_2 + 3Inl + 2H_2O .$$

where Ind = indoline and Inl = indole.

The direct synthesis of the anilides RCONHPh from an aromatic nitro-compound and organic acids RCOOH can be achieved by employing molybdenum carbonyl.[233] Depending on the substituent, the yield of anilides ranges from 46 to 85%. The reaction is selective with respect to the nitro-group; the C=C bond and the OH, C=O, OCH_3, COOH, NH_2, CN, etc. groups are not reduced. In the presence of another catalyst, namely $RuCl_2(PPh_3)_3$, and added triethylamine, aniline was obtained under the same conditions.[234] The $PtCl_2(PPh_3)_2 + SnCl_2$ system exhibits activity in the reductive acylation of aromatic nitro-compounds in a CO atmosphere:[235]

$$PhNO_2 + RCOOH + 3CO \rightarrow PhNHCOR + 3CO_2 .$$

$SnCl_4$ can be replaced here by other Lewis acids.

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Thus one may conclude that the use of coordination compounds in the chemistry of aromatic nitro-compounds is developing vigorously; this has made it possible to obtain complexes with a fundamentally new structure and complex catalysts effective and selective in reduction reactions can be created on the basis of theoretical ideas. It is likely that coordination compounds based on aromatic nitro-compounds may possess interesting biological properties (see, for example, Nishida et al.[236]).

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