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Non-traditional Oxidants in Preparative Coordination Chemistry

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The application of nitrosonium and arenediazonium salts, carbenium, silver(I), and mercury(II) ions, protic acids, and amine oxides as oxidants in preparative coordination chemistry is examined. Specific examples illustrate which problems in the field of the synthesis and reactions of coordination compounds can be solved with the aid of these oxidants.
The bibliography includes 158 references.

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I. INTRODUCTION

Many synthetic methods are based on the use of oxidants in preparative coordination chemistry, among which oxidants, one may include the halogens, oxygen, hydrogen peroxide, concentrated nitric acid, permanganates, bromates, persulphates, etc. The choice of oxidants depends on the problem to be solved. It is sometimes required to oxidise the central atom of a complex without affecting the ligand, while in other cases it is necessary to oxidise the ligand without affecting the central atom. The products of the reduction of oxidants are frequently themselves ligands, which is sometimes a decisive factor in the choice of the oxidant. The larger the set of oxidants available to the synthetic chemist, the easier it is to solve specific problems.

In the last 10–15 years the range of oxidants in coordination chemistry has been greatly expanded by the use of non-aqueous solvents. The solvent as a rule influences strongly the oxidation-reduction potential of the system. One of the causes of this behaviour is the different degrees of solvation of the oxidant molecule and its reduction products. For example, the high oxidation potential of chlorine in polar solvents is associated, in particular, with the much higher solvation energy of two chloride ions than that of the Cl_2 molecule, which tends to shift the equilibrium to the right in the presence of the solvent. In [weakly] solvating solvents the difference between the solvation energies of the chlorine molecule and chloride ions is smaller and this is reflected in a decrease of the oxidation potential. In practice this amounts to the observation

that chlorine becomes a milder oxidant in a weakly solvating solvent. Thus, attempts[1] to obtain platinum(IV) complexes of hydroxylamine by oxidising $[Pt(NH_2OH)_2X_2]$ (X = Cl or Br) by halogens in an aqueous solution led to the decomposition of the coordinated NH_2OH molecule and the formation of acido- and hydroxo-complexes of platinum(IV). When this reaction was carried out in the weakly solvating CCl_4, the corresponding platinum(IV) complexes with coordinated hydroxylamine were obtained.

In recent years oxidants which may be referred to as non-traditional have been introduced into preparative chemistry to an increasing extent. The term "new oxidants" would not be altogether accurate since individual instances of their use have been known for a fairly long time. The fact that the oxidants considered in this review are sometimes fairly specific in the oxidation of particular ligands in coordination compounds is of special interest to synthetic chemists. They make it possible to direct the oxidation process to a specific site in the complex.

II. NITROSONIUM SALTS

Nitrosonium salts are one-electron oxidants which have been most frequently used during the last decade. According to Mussini[2] and Schmid and Neumann,[3] the redox potential of the NO^+/NO pair in aqueous solution is 1.45 V (1.23 V relative to the Ag/AgCl electrode). When nitrosonium salts are used in non-aqueous solvents with weak electron-donating properties, the difference between the degrees of solvation of NO^+ and NO diminishes and the activity in relation to oxidation reactions increases.[4] Indeed, the potential of the NO^+/NO pair in nitromethane relative to the Ag/AgCl electrode is as much as 1.58 V.[5]

Various methods of preparation of the above reagents are known. Nitrosyl chloride NOCl is formed on direct interaction of Cl_2 and NO, in the reaction of $NOHSO_4$ or $NaNO_2$ with HCl, and also as one of the products of the reaction of KCl and NO_2; NOBr is usually obtained from Br_2 and NO.[6] In the same study a method of synthesis of nitrosyl fluoride was also described. Among the different procedures for the preparation of $NO^+BF_4^-$,[7-11] the method based on the reaction of N_2O_3 with aqueous HBF_4 solution is most often employed:[9-11]

$$N_2O_3 + 2HBF_4 \rightleftarrows 2NO^+BF_4^- + H_2O,$$

$NO^+ClO_4^-$ is obtained analogously.[11-14]

Nitrosonium salts containing large anions with a weak electron-donating capacity are used to synthesise various metal salts and homogeneous solvato-complexes. Thus, one of the first syntheses in which a nitrosonium salt was used as the oxidant was achieved in 1950:[15]

$$Na + NO^+SbCl_6^- \xrightarrow{SO_2} Na[SbCl_6] + NO.$$

Later the oxidation of metals by nitrosonium salts in electron-donating solvents came to be used in the synthesis of homogeneous solvato-complexes. Thus, the complexes $[Cu(MeCN)_4]X$ [16,17] have been obtained by oxidising copper in acetonitrile with NO^+X^- (X = BF_4 or ClO_4); the perchlorate $NO^+ClO_4^-$ in MeCN is capable of oxidising metallic gold with formation of the complex $[Au(MeCN)_4](ClO_4)$.[18] The solvates $[Eu(MeCN)_n]X_3$ (X = BF_4 or PF_6),[19] $[Ni(MeCN)_6](ClO_4)_2$,[20] and $[Pd(MeCN)_4](BF_4)_2$ [21,22] have been synthesised by oxidising metals with nitrosonium salts.

The oxidation of the complex $[Re_2Cl_4(PMe_2Ph)_4]$ with metal–metal bonds by one mole of $NO^+PF_6^-$ in acetonitrile led to the formation of $[Re_2Cl_4(PMe_2Ph)_4](PF_6)$ in 73% yield. The complex $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ has been isolated in 90% yield as a result of the interaction of the initial compound with 3.5 moles of $NO^+PF_6^-$.[23]

The oxidation of the complexes $[Cr(NO)(CNCMe_3)_4(PR_3)]X$, where R = Et or Bu, by NO^+X^- salts (X = BF_4 or PF_6) in acetone is completed after 10 min with the formation of the products $[Cr(NO)(CNCMe_3)_4(PR_3)]X_2$ in approximately 90% yield.[24] The reaction of the zerovalent platinum complex $[Pt(PPh_3)_2(C_2H_4)]$ with nitrosonium tetrafluoroborate in acetonitrile led to the oxidation of the central atom with the simultaneous substitution of the coordinated ethylene by solvent molecules:[25]

$$[Pt(PPh_3)_2(C_2H_4)] + 2NO^+BF_4^- + 2MeCN \rightarrow$$
$$\rightarrow [Pt(PPh_3)_2(MeCN)_2](BF_4)_2 + C_2H_4 + 2NO.$$

The oxidation of the complex $MoL(NO)(CO)_2$ [L = tris(3,5-dimethylpyrazolyl)borate] by nitrosyl chloride is accompanied by substitution of the coordinated carbonyl groups by chloride ions:[26]

$$MoL(NO)(CO)_2 + 2NOCl \xrightarrow{CH_2Cl_2} MoL(NO)Cl_2 + 2CO + 2NO.$$

In the above examples the substitution of the ligands by the nitrosyl group was not noted. However, a series of studies have produced data indicating a dual reactivity of nitrosonium salts towards metal complexes. It has been established that the NO^+ cation can react to give either the corresponding nitrosyl derivatives or oxidation products. Sometimes both processes take place simultaneously. It has been shown[27,28] that the product of the reaction of $Mo(CO)_6$ with NO^+ in acetonitrile may be different under different experimental conditions. Thus, when the NO formed in the reaction is removed from the reaction mixture, the complex $[Mo(NO)(MeCN)_5]^{2+}$ is obtained, whereas, in the case where the reaction is carried out in the presence of NO, $[Mo(NO)_2(MeCN)_4]^{2+}$ is isolated. When these investigations were continued, it was established[29] that, when the reaction between $[Cr(CO)_4L]$ [L = bis(diphenylphosphino)-methane (Dppm) or 1,2-bis(diphenylphosphino)ethane (Dppe)] and $NO^+BF_4^-$ in CH_2Cl_2 is carried out in a closed nitrogen-filled flask, the product is the complex $[Cr(CO)_3(NO)L]^+$. On the other hand, when NO is removed from the reaction sphere by bubbling nitrogen through the reaction mixture, the oxidation product $[Cr(CO)_4L]^+$ is formed. The studies carried out by Connelly's group led to the mechanism

$$[ML_n] + NO^+ \rightarrow [ML_n(NO)]^+ \begin{cases} \rightleftarrows [ML_n]^+ + NO; \\ \rightarrow [ML_{n-1}(NO)]^+ + L. \end{cases}$$

The mechanism illustrates the fact that a change in reaction conditions can shift the equilibrium and can lead to the possibility of obtaining either the oxidation product $[ML_n]^+$ or the substituted nitrosyl complex $[ML_{n-1}(NO)]^+$. The latter can also be regarded as the oxidation product when the coordinated nitrosyl is converted into the NO^- anion. It has been stressed[29] that the nature of the central atom M and of the coordinated ligand L can appreciably affect the equilibrium position. The ability of the complex $[ML_n]$ to form intermediates of the type $[ML_n(NO)]^+$ with an increased coordination number is also important.

The interaction of the complex $(Et_4N)[V(CO)_6]$ with $NO^+BF_4^-$ in dichloromethane, resulting in the formation of the substituted complex $[V(CO)_5(NO)]$ has been investigated.[30]

It has been shown that the infrared spectra of the products obtained by the interaction of $[V(CO)_6]^-$ with NO^+ and of $V(CO)_6$ with NO are identical. The following reaction mechanism has been proposed:[18]

$$V(CO)_6^- + NO^+ \rightarrow V(CO)_6 + NO \rightarrow [V(CO)_6(NO)] \xrightarrow{-CO} [V(CO)_5(NO)].$$

This mechanism does not conflict with Connelly's mechanism and actually supplements it.

We shall quote certain examples illustrating the dual reactivity of nitrosonium salts. When the isonitrile complex of tungsten $W(CNPh)_2$ is mixed with $NO^+PF_6^-$ in tetrahydrofuran (THF), two products are formed:[31]

$$2W(CNPh)_6 + 2NO^+PF_6^- \xrightarrow{THF} [W(NO)(CNPh)_5](PF_6) + [W(CNPh)_7](PF_6) + NO.$$

The oxidation of the osmium complex $[Os(CNR)_4X_2]$ proceeds without the formation of substitution products:[32]

$$[Os(CNR)_4X_2] + NO^+BF_4^- \xrightarrow{MeCN} [Os(CNR)_4X_2](BF_4) + NO;$$
R = t-Bu, iso-Pr, C_6H_{11}; X=Cl, Br.

The interaction of a solution of $Mo(CO)_6$ in dichloromethane with $NO^+PF_6^-$ leads to the formation of $Mo(NO)_2(PF_6)$, which has a polymeric structure with a bridging hexafluorophosphate ligand.[33] The corresponding solvates $[Mo(NO)_2S_n].(PF_6)_2$ (S = solvent molecule) are formed from the same reactants in MeCN [34] or $MeNO_2$.[33]

It has been noted[35–38] that nitrosonium salts can react in two ways also with cluster compounds. For example, the oxidation of the anion $[Os_4H_3(CO)_{12}]^-$ by the NO^+X^- salts (X = BPh_4 or PF_6) in acetonitrile gave rise to the clusters $[Os_4H_3(CO)_{12}(MeCN)_2]X$ in a yield of ~35%. The replacement of acetonitrile by dichloromethane or THF results in the formation of the compound $[Os_4H_3(CO)_{12}(NO)]$ in this reaction.[38]

It has been noted in a review[35] that nitrosyl salts are used as the source from which the nitride ligand is introduced into the carbonyl clusters of various metals.

The ability of nitrosonium salts to oxidise the coordinated azide ion is used in practice in preparative coordination chemistry:

$$[Co(NH_3)_5N_3](ClO_4)_2 + NO^+ClO_4^- \xrightarrow{S} [Co(NH_3)_5S](ClO_4)_3 + N_2O + N_2,$$

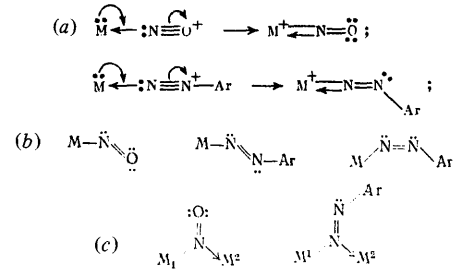
where S = tetramethylene sulphone,[39] triethyl phosphate,[40] or acetonitrile.[41,42] The reaction led to the isolation of gaseous oxidation-reduction products, the vacant site in the coordination sphere being occupied by solvent molecules.

The reaction between the phosphine complexes of nickel(II) $[Ni(PPh_3)_2X_2]$ (X = Cl, Br, or NO_3) and NOCl has been investigated[43,44] in a benzene–cyclohexane mixture. Without dwelling on the pathways leading to the formation of the oxidation products, the authors conclude that the reaction results in the formation of the dimers, $[Ni(OPPh_3)XCl]_2$.

III. ARENEDIAZONIUM SALTS

The classical studies by Nesmeyanov and co-workers[45] were devoted to the oxidation and arylation of organometallic compounds, especially of ferrocene by arenediazonium salts.

Certain aspects of the coordination chemistry of arenediazonium have been examined in a review[46] and an analogy has been drawn between the nitrosyl and arenediazenate complexes of transition metals. This applies in broad outline to the valence structures of the complexes in linear (a), angular (b), and bridged (c) coordination, i.e.



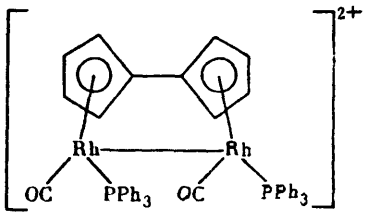
and also to the similarity of the reactivities. The analogy has been extended[29,47] to redox reactions with participation of nitrosonium and arenediazonium salts.

It has been noted[47] that there are no literature data on the oxidation potentials of nitrosonium and diazonium in any one non-aqueous solvent, i.e. under comparable conditions. However, it follows from the available potentials that NO^+ (1.58 V, nitromethane, Ag/AgCl electrode) is a stronger oxidant than ArN_2^+ (0.295 V, sulpholan, saturated calomel electrode), although strictly speaking the potentials quoted are not directly comparable. A comparative study has been made of the interaction of the complexes $[Cr(CO)_2L.(\eta\text{-}C_6Me_6)]$ [L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OPh)_3$, or $P(OMe)_3$] with $NO^+PF_6^-$ and $PhN_2^+PF_6^-$ in PhMe–MeOH and CH_2Cl_2 respectively.[47] It has been established that nitrosonium salts give rise only to the products of substitution of CO or L, i.e. $[Cr(CO)(NO)L(\eta\text{-}C_6Me_6)](PF_6)$ and $[Cr(CO)_2(NO)(\eta\text{-}C_6Me_6)](PF_6)$. The interaction with a diazonium salt leads to the formation, together with the substitution products $[Cr(CO)(N_2Ph)L(\eta\text{-}C_6Me_6)](PF_6)$ and $[Cr(CO)_2(N_2Ph)(\eta\text{-}C_6Me_6)](PF_6)$, also of the one-electron oxidation product $[Cr(CO)_2L(\eta\text{-}C_6Me_6)](PF_6)$. In order to account for this finding, the authors[29,47] turned to the mechanism of the interaction of carbonyl complexes with nitrosonium salts which they proposed (see previous Section). On the basis of the similarity between the reactivities of NO^+X^- and $ArN_2^+X^-$, they extended the scheme to the reactions of complexes of the type $[ML_n]$ with $ArN_2^+X^-$. Analysis showed, despite the more negative potential of the ArN_2^+/ArN_2 pair compared with that of the NO^+/NO pair, diazonium salts are more reactive one-electron oxidants. On the one hand, this can be explained by the greater steric hindrance by the ArN_2^+ ligand to the formation of the intermediate $[ML_n(ArN_2)]^+$ and on the other, the formation of the oxidation product $[ML_n]^+$ is favoured by the irreversible formation of N_2 and biaryl:

$$2ArN_2^+ + 2e \rightarrow 2N_2 + Ar\text{—}Ar.$$

The oxidising capacity of diazonium salts can be used in preparative coordination chemistry. Thus the complex $[Mo(NO)(MeCN)(Dppe)_2](PF_6)$ has been oxidised by the stoichiometric amount of $[p\text{-}FC_6H_4N_2]^+(PF_6)^-$ in dichloromethane.[48] The reaction is completed in 30 min; $[Mo(NO).(MeCN)(Dppe)_2](PF_6)_2$ was isolated from the reaction mixture in 92% yield. The one-electron oxidation product $[Co(Salen)(H_2O)](BF_4)$ (H_2Salen is the Schiff base prepared from one mole of ethylenediamine and two moles of salicylaldehyde) has been obtained by the reaction of [Co(Salen)] with $[p\text{-}XC_6H_4N_2]^+(BF_4)^-$ (X = H, OMe, or NO_2) in CH_2Cl_2 or Me_2CO containing traces of water.[49] It has been stated[50] that diazonium salts in acetonitrile are capable of oxidising metallic copper or silver with formation of the corresponding homogeneous solvato-complexes. The oxidation can involve also coordinated ligands. Thus the interaction of $[Rh(CO)(PPh_3)(\eta\text{-}Cp)$ (Cp = cyclopentadienyl)

with $[p\text{-}FC_6H_4N_2]^+(BF_4)^-$ in dichloromethane leads to the formation of the fulvalene complex:[51]



IV. TRIPHENYLCARBENIUM SALTS

In 1958 it was suggested[52] that triphenylcarbenium salts (the Ph_3C^+ cation is frequently referred to as the trityl cation in the literature) be used as powerful acceptors of hydride ions. The employment of $Ph_3C^+X^-$ in preparative coordination chemistry can be considered in terms of at least three aspects. Firstly, trityl is used as a one-electron oxidant. Secondly, it is capable of abstracting the hydride ion from an organic ligand. Thirdly, triphenylcarbenium salts are able to accept a coordinated hydride ion.

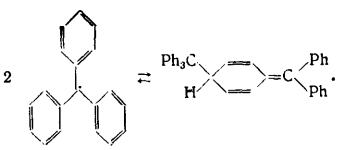
Data concerning the synthesis of triphenylmethyl perchlorate and triphenylmethyl tetrafluoroborate have been published.[53,54] The above reagents are obtained by the reaction of triphenylmethylmethanol with 71% $HClO_4$ or 48% HBF_4 in the presence of acetic anhydride. The latter is introduced to remove water:

$$Ph_3COH + H^+ \rightarrow Ph_3C^+ + H_2O.$$

The yields are 76 and 92% respectively. The tetrafluoroborate $Ph_3C^+BF_4^-$ has advantages over the perchlorate $Ph_3C^+ClO_4^-$ because of its greater stability.[53]

It has been established[50] that $Ph_3C^+BF_4^-$ can function as a one-electron oxidant and is able to oxidise metallic copper with formation of the homogeneous solvato-complex $[Cu(MeCN)_4](BF_4)$. The phosphine complexes of palladium(II) $[Pd(PPh_3)_4]X_2$ (X = BF_4 or PF_6) and $\{Pd[P(OPh)_3]_4\}.(PF_6)_2$ have been synthesised in 60 and 50% yields respectively by the oxidation of the complexes $[Pd(PPh_3)_4]$ and $\{Pd[P(OPh)_3]_4\}$ by the trityl cation.[55]

The triphenylmethyl radical, formed in the reduction process, dimerises with formation of 1-diphenylmethylene-4-tritylcyclohexa-2,5-diene:[56,57]



The one-electron oxidation of the complex $\{CpW(NO).[P(OMe)_3]\}$ with triphenylcarbenium tetrafluoroborate in CH_2Cl_2 in air led to the isolation from the reaction mixture of the already known[59] compound $Ph_3COOCPh_3$ in 13% yield.[58] Cobalt(II) complexes having the general formula $[CoHL_4]X$ [L = $P(OEt)_2Ph$, $P(OMe)_2Ph$, or $P(OPh)_3$; X = PF_6 or BF_4] have been obtained by the reaction of the corresponding hydrides $[CoHL_4]$ with a stoichiometric amount of the triphenylcarbenium salt.[60] In this case the trityl cation behaves as a one-electron oxidant and not as a hydride ion acceptor. This has been explained[60] by the greater strength of the Co–H bond.

The dependence of the reactivity of the triphenylcarbenium ion on the properties of the solvent has been clearly demonstrated in a study of the reaction of $Ph_3C^+PF_6^-$ with the polyhydride $Re_2H_8(PPh_3)_4$.[61] The abstraction of a hydride ion in acetonitrile results in the formation of a coordination-saturated intermediate, which is stabilised in the form of the solvato-complex $[Re_2H_7(PPh_3)_4(MeCN)](PF_6)$. When the reaction is carried out in dichloromethane, $Ph_3C^+PF_6^-$ functions as a one-electron oxidant, which results in the formation of $[Re_2H_8(PPh_3)_4](PF_6)$.

Other carbenium ions can be used in one-electron oxidation reactions in addition to the triphenylmethyl cation. Thus the complex $\{CpW(NO)[P(OMe)_3]\}$ is oxidised to the corresponding monocationic complex on interaction with $MeOSO_2F$ in accordance with the reaction equation

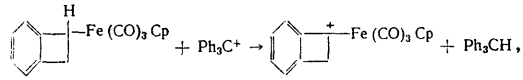
$$[CpW(NO)\{P(OMe)_3\}] + MeOSO_2F \xrightarrow{CH_2Cl_2} \rightarrow [CpW(NO)\{P(OMe)_3\}](OSO_2F) + {}^1/_2C_2H_6.$$

The ethane evolved was detected by gas–liquid chromatography (GLC).[58]

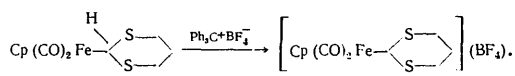
The one-electron oxidation of the complex $[MoCl_2(Dppe)_2]$ by the compound $[Et_3O]^+(BF_4)^-$ and $MeOSO_2F$ in dichloromethane leads to the formation of the molybdenum(III) complex $[MoCl_2(Dppe)_2]X$ (X = BF_4 or OSO_2F).[62] Triethyloxonium tetrafluoroborate oxidises $[Re(CO)_3Cl(PPh_3)_2]$ to the corresponding complex $[Re(CO)_3Cl(PPh_3)_2](BF_4)$. Although the reduction products were not identified in the above study,[62] by analogy with other data[58] one can assume that the Me^+ and Et^+ ions are reduced as a result of the reaction.

A brief survey of the applications of triphenylcarbenium salts in the chemistry of organometallic compounds has been published.[63] We shall quote only a few additional examples.

The reaction



has been carried out.[64] The carbene complex has been isolated analogously in the oxidation of the dithiane derivative:[65]



A μ-methylidyne compound is formed from a complex with a bridging methylene ligand:[66,67]

$$[Cp_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH_2)] + Ph_3C^+PF_6^- \xrightarrow{CH_2Cl_2} \rightarrow [Cp_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH)](PF_6) + Ph_3CH.$$

The initial complex can be regenerated by treating the final product with $Li[HBEt_3]$.

The question of the mechanism of hydride shifts has been the subject of a controversy. It has been noted in a monograph[68] that the hydride shift reaction can take place in either one or two steps:

$$B^+ + H{-}A \rightarrow BH + A^+;$$
$$B^+ + H{:}A \rightarrow B^{\cdot} + [HA]^{\cdot+} \rightarrow BH + A^+$$

In several studies the possibility of a hydride shift via a mechanism involving a one-electron transfer has been demonstrated. The question of the extent to which this mechanism occurs has so far remained open.[68]

The ability of the trityl cation to interact with an inner-sphere hydride ion can be clearly demonstrated in relation to the complex $[RuH_2(PPh_3)_4]$.[69] Treatment of the complex with a calculated amount of $Ph_3C^+PF_6^-$ yielded $[RuH(PPh_3)_4].(PF_6)$. Oxidation of the hydride ligand can lead to the

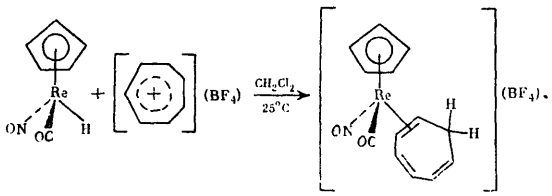
formation of the bridged complex[70]

$$2\,(Ph_4As)\,[HCr(CO)_5] + Ph_3C^+BF_4^- \xrightarrow{THF} \rightarrow (Ph_4As)\,[(CO)_5Cr(\mu\text{-}H)Cr(CO)_5] + Ph_3CH + [Ph_4As](BF_4).$$

It has been demonstrated convincingly[71] that the character of the product of the reaction between $Ph_3C^+X^-$ ($X = BF_4$ or PF_6) and the hydride compound $[CpW(NO)_2H]$ depends on the electron-donating capacity of the solvent. Thus the solvato-complex $[CpW(NO)_2(MeCN)]X$ is formed in acetonitrile, while the dimer $[Cp_2W_2(NO)_4H]$ is produced in dichloromethane, which has no electron-donating properties. The oxidation of the hydride ligand in the complexes $\{Mn(CO)_3[P(OMe)_3]_2H\}$ [72] and $[Cp(CO)_3MH]$ ($M = Mo$ or W) [73] by $Ph_3C^+PF_6^-$ in CH_2Cl_2 leads to the deposition of the compounds $\{Mn(CO)_3[P(OMe)_3]_2(FPF_5)\}$ and $[Cp(CO)_3M.(FPF_5)]$ respectively in the solid phase. These compounds are formed because the solvent cannot compete with the PF_6^- anion for a site in the inner coordination sphere. The reaction of the rhenium complex $[CpRe(CO)(NO)H]$ with triphenylcarbenium tetrafluoroborate in CH_2Cl_2 affords $[CpRe(CO)(NO)(\eta_2\text{-}PhCHPh_2)](PF_6)$ as the final product.[74]

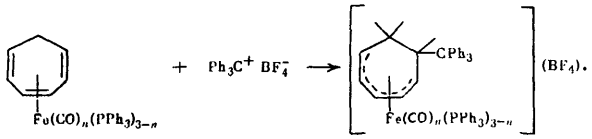
Apart from trityl cations, other carbenium ions can also be used as hydride ion acceptors in preparative coordination chemistry. Although the tropylium cation is a much less active hydride ion acceptor than the triphenylcarbenium cation,[68] nevertheless the oxidation of the cluster anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ by the tropylium ion has been described.[75] This reaction involves the abstraction of the hydride ligand and the formation of the compound $[Re_3(\mu\text{-}H)_3(CO)_{10}L_2]$ in the presence of carbon monoxide ($L = CO$) or an electron-donating solvent ($L = MeCN$). In the absence of electron donors, in the inert dichloromethane, the complex $[Re_3H_2(CO)_{10}(\eta_5\text{-}C_7H_9)]$ is formed in a satisfactory yield.

The interaction of tropylium tetrafluoroborate with the complex $[CpRe(CO)(NO)H]$ leads to the dehydrogenation of the complex and subsequent coordination of the triene formed:[76]



Dehydrogenation of the complex $[CpOs(CO)_2H]$ by tropylium tetrafluoroborate in CH_2Cl_2 at 25 °C for 6 days gives rise to $[CpOs(CO)_2(1,2\text{-}\eta_2\text{-}C_7H_8)](BF_4)$ in 80% yield.[77]

In conclusion of this Section, we may note that the trityl cation can alkylate coordinated ligands, for example:[78,79]



V. PROTIC ACIDS

In studies in non-aqueous solvents the proton can function as a one-electron oxidant. Thus metallic titanium or chromium are oxidised by HBF_4 in acetonitrile with formation of $[Ti(MeCN)_6](BF_4)_3$ and $[Cr(MeCN)_x](BF_4)_3$.[80] When zerovalent molybdenum hexacarbonyl $Mo(CO)_6$ was refluxed with anhydrous formic acid for 3 h in diglyme, $Mo_2(O_2CH)_4$ was isolated in 65% yield.[81] The complex $[CpRh(PPh_3).(PhC_2Ph)]$ reacts with an excess of trifluoroacetic acid at 40 °C with displacement of the acetylenic ligand and the formation of the oxidation product $[CpRh(PPh_3)(O_2CCF_3)]$.[82]

The reaction of the dimeric complex $[CpCr(NO_2)]_2$ with two moles of HBF_4OMe_2 in dichloromethane leads to oxidative cleavage with formation of the monomeric compound $CpCr(NO)_2BF_4$, which is converted into the stable complex $[CpCr(NO)_2(MeCN)](BF_4)$ on treatment with acetonitrile.[9] Similarly the interaction of the isoelectronic complex $[CpFe(CO)_2]_2$ with toluene-*p*-sulphonic acid in acetonitrile leads to oxidative cleavage of the Fe–Fe bond and formation of the solvato-complex $[CpFe(CO)_2(MeCN)](O_3SC_6H_4Me)$.[84] It was assumed in the above study that the protic acid is in fact responsible for the oxidation of the complex. However, the evolution of free hydrogen was not observed.

Together with triphenylcarbenium and silver salts, protic acids are used to oxidise the H^- ion in hydride complexes. It has been established[85] that $MoH_4(PMePh_2)_4$ reacts with HBF_4 or HBF_6 in THF to form the cation $[MoH_3(PMePh_2)_3]^+$. The reactions with the weaker acids CF_3CO_2H or $p\text{-}MeC_6H_4SO_3H$ in toluene lead to the formation of the compounds $[MoH_2(CF_3CO_3)_2(PMePh_2)_3]$ and $[MoH_2.(p\text{-}MeC_6H_4SO_3)_2(PMePh_2)_3]$. The complex $[CpW(NO)_2H]$ is oxidised by anhydrous toluene-*p*-sulphonic acid in THF to $[CpW(NO)_2(OSO_2C_6H_4Me)]$.[86] The interaction of the complex $[H_2RhCp(PPr_3)]$ with trifluoroacetic acid in methanol in the presence of NH_4PF_6 entails a rapid reaction accompanied by the evolution of hydrogen and the formation of the dinuclear complex $[Cp(PPr_3)Rh(\mu\text{-}H)_3Rh(PPr_3)Cp](PF_6)$.[82] The interaction of tungsten, rhenium, osmium, and iridium polyhydride compounds with $HBF_4.OEt_2$ in acetonitrile has been investigated.[87] The initial compounds and the final products of the syntheses are presented schematically below:[87]

$$WH_6(PMe_2Ph)_3 \rightarrow [WH_2(MeCN)_3(PMe_2Ph)_3]^{2+};$$
$$ReH_5(PMe_2Ph)_3 \rightarrow [ReH(MeCN)_3(PMe_2Ph)_3]^{2+};$$
$$ReH_7(PPh_3)_2 \rightarrow [ReH(MeCN)_4(PPh_3)]^{2+};$$
$$OsH_4(PMe_2Ph)_4 \rightarrow [Os(MeCN)_3(PMe_2Ph)_3]^{2+};$$
$$IrH_5(PPh_3)_2 \rightarrow [IrH_2(MeCN)_2(PPh_3)_2]^+.$$

The authors concluded[87] that the central atoms in the complexes $WH_6(PMe_2Ph)_3$ and $ReH_7(PPh_3)_2$ have the d^0 electronic configuration. The protonation of the metal ion in such compounds is therefore hardly to be expected. It is most likely that the interaction with H^+ leads to the formation of the $M...H...H^+$ linear intermediate. On the other hand, the complexes $OsH_4(PMe_2Ph)_3$, $ReH_5(PMe_2Ph)_3$, and $IrH_5.(PPh_3)_2$ are more likely to be protonated at the metal atom. In all cases the protonated adducts are relatively unstable and decompose at room temperature with evolution of hydrogen and the vacant sites generated in the inner sphere are filled by solvent molecules. In the analysis of their own experimental and literature data on the acidolysis of the polyhydride compounds the authors[87] note that the biscationic complex is frequently stabilised as a result of the reaction. However, the causes of this phenomenon remain unelucidated.

The interaction of $[Mn(CO)_5]^-$ with trifluoromethanesulphonic acid in THF yielded the compound $HMn(CO)_5$,[88] which is a fairly strong acid ($pK_a = 7$).[89] Consequently, the hydrogen in $HMn(CO)_5$ has almost no hydride character. Nevertheless, the interaction of the complex $[(Ph_3P)_2N].[Mn(CO)_5]$ in the absence of a solvent with pure CF_3SO_3H leads to the formation of the complex $Mn(CO)_5(SO_3CF_3)$ and

the evolution of hydrogen.[89] This reaction proceeds via the stage

$$HMn(CO)_5 + CF_3SO_3H \rightarrow Mn(CO)_5(SO_3CF_3) + H_2.$$

Thus, when the character of the medium is altered, a ligand, which does not exhibit the properties of a hydride in other solutions, is oxidised.

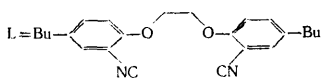
VI. SILVER AND MERCURY SALTS

The importance of silver salts as dehalogenating agents has been emphasised in a review.[90] However, the salts AgX are also used as one-electron oxidants in syntheses in non-aqueous media. According to Rabinovich and Khavin,[91] the redox potential of the Ag^+/Ag pair in aqueous solution is 0.799 V. There are no literature data on the redox potentials of the Ag^+/Ag pair in weakly electron-donating solvents. This can probably be accounted for by the limited solubility of silver salts in such media.[92] In order to estimate the oxidising capacity of $AgBF_4$ in non-aqueous solvents, its reactions with $N(C_6H_4Br\text{-}p)_3$ (E = 1.16 V), NPh_3 (E = 0.88 V), and Cp_2Fe (E = 0.38 V) were investigated[92] in CH_2Cl_2, PhMe, MeCN, and THF. In all the solvents, ferrocene is oxidised to $[Cp_2Fe](BF_4)$, whereas amines are oxidised only by a suspension of $AgBF_4$ in dichloromethane. Consequently $AgBF_4$ is a powerful oxidant in CH_2Cl_2, but is milder in PhMe, MeCN, and THF, in agreement with their solvating capacities.

An important additional factor responsible for the application of silver salts in synthesis as oxidants is the possibility of the ready separation of the metallic silver formed on reduction from the reaction mixture. As a rule, reactions with participation of Ag^+ as the oxidant are rapid, are satisfactorily selective, and do not require an appreciable excess of this reagent.

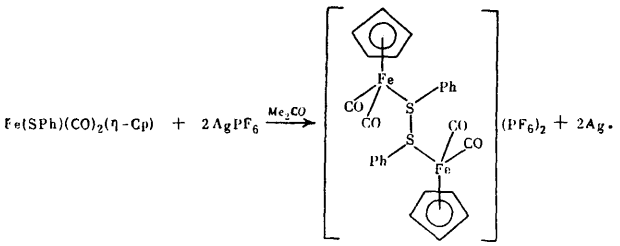
A manual recommends[53] that silver tetrafluoroborate be obtained from AgF and BF_3 by the method of Olah and Quinn.[93] The same compound can also be obtained by dissolving silver oxide in 45% HBF_4.[94] Silver perchlorate is obtained by the reaction of Ag_2CO_3 with 10% $HClO_4$. The synthesis involves filtration, the removal of water *in vacuo*, and azeotropic drying with benzene.[53]

The Ag^+ ion has been used in preparative coordination chemistry for a long time. For example, as early as 1923 Morgan[95] suggested that the complex $[Cu(MeCN)_6](NO_3)$ be prepared by oxidising metallic copper with $AgNO_3$ in acetonitrile. The extensive use of silver salts as oxidants began in the last decade. According to Treichel and Essenmacher,[96] the isonitrile complex of chromium $[Cr(CNPh)_6]$ is instantly oxidised in acetone by one equivalent of $AgPF_6$ with formation of $[Cr(CNPh)_6](PF_6)$. When the latter was allowed to interact with yet another equivalent of $AgPF_6$ or on interaction of the initial complex with two moles of silver hexafluoroborate, $[Cr(CNPh)_6](PF_6)_2$ was obtained. The chelate compounds $[CrL_3](PF_6)$ and $[CrL_3](PF_6)_2$ have been synthesised analogously:[97]



The oxidation of the complex $CpCo(PPh_3)_2$ by silver halides AgX (X = Cl, Br, or I) in THF led to the formation of the compounds $[CpCo(PPh_3)X]$.[98]

The oxidative dimerisation reaction, which proceeds via the oxidation of the ligand, has been investigated:[99]



The authors[99] suggest that the HOMO in the initial complex is localised mainly on the sulphur atom and not on the iron atom. The loss of one electron from this orbital leads to the formation of a radical species with the unpaired electron localised on the ligand. The final dimeric complex is formed from two such species. The central atom in the complexes $Fe(SPh)(CO)L(\eta\text{-}C_5R_5)$ is oxidised:

$$Fe(SPh)(CO)L(\eta\text{-}C_5R_5) + AgX \rightarrow [Fe(SPh)(CO)L(\eta\text{-}C_5R_5)]X + Ag;$$
$$R=Me,\ L=CO,\ PMe_3,\ PMe_2Ph,\ PMePh_2;$$
$$R=H,\ L=PMe_3,\ PMe_2Ph,\ PMePh_2.$$

Numerous examples of the oxidation of organometallic compounds with silver salts have been described in a book.[100]

The possibility of the oxidation of the hydride complexes $[MoH_4L_4]$ (L = PMe_2Ph or $PMePh_2$) by silver tetrafluoroborate in acetonitrile has been demonstrated:[101]

$$[MoH_4L_4] + 2AgBF_4 + 2MeCN \rightarrow [MoH_2L_4(MeCN)_2](BF_4)_2 + H_2 + 2Ag.$$

The reactions reached completion in several minutes and the products were obtained in satisfactory yields.

Mercury salts together with silver salts can be used in experiments in non-aqueous solvents as oxidants. Like the Ag^+ ion, the Hg^{2+} ion has a relatively high oxidising capacity. In both cases the reduction products, namely metallic silver and mercury, can be readily separated from the reaction mixture. The oxidation of the lanthanides Sm, Er, Yb,[102] Sc, and Y [103] by $HgCl_2$ in THF yielded the tetrahydrofuranates of the corresponding trichlorides:

$$2Ln + 3HgCl_2 + 6THF \rightarrow 2LnCl_3 \cdot 3THF + 3Hg.$$

The complex $[Cr(CO)_5(O_2CCF_3)]^-$ is formed as a result of oxidative substitution by mercury trifluoroacetate:[104]

$$[Cr_2(CO)_{10}]^{2-} + Hg(O_2CCF_3)_2 \rightarrow 2[Cr(CO)_5(O_2CCF_3)]^- + Hg.$$

VII. AMINE OXIDES

The ability of the CO_2 molecule to be coordinated to metal ions is known to be appreciably weaker than that of carbon monoxide. For this reason, one of the methods of the specific elimination of CO from metal carbonyl compounds involves the oxidation of a carbonyl ligand to CO_2 with subsequent substitution of this molecule by some stronger electron donor (in particular, a solvent molecule). Trimethylamine oxide is nowadays used widely for the oxidation of the coordinated CO molecule.

The above reagent is formed in 95% yield as the dihydrate $Me_3NO.2H_2O$ on oxidation of Me_3N by hydrogen peroxide:[105,106]

$$Me_3N + H_2O_2 + H_2O \rightarrow Me_3NO \cdot 2H_2O.$$

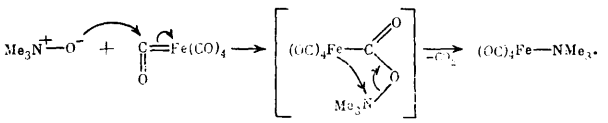
Total dehydration gives rise to the extremely hygroscopic product Me_3NO.[106,107] The ability of amine oxides to react with metal carbonyls was first demonstrated by Heiber and Lipp[108] and Alper and Edward.[109] In particular, it has been

established[109] that aliphatic, aromatic, or heterocyclic amine oxides are reduced to the corresponding amines on interaction with $Fe(CO)_5$. The amines have been isolated from the reaction mixture and characterised. Iron oxides have also been obtained in the synthetic reactions. It was suggested in 1974 [110] that the reactions of amine oxides with metal carbonyls be used for the decomposition of the complex and the isolation of the organic ligand. Thus, when the complexes $[LFe(CO)_3]$ [L = C_8H_8, norbornadiene,[110] or $C_7H_6NN(H)C_6H_4NO_2$ [111]] in benzene or acetone react with an excess of Me_3NO or $Me_3NO.2H_2O$, complete decarbonylation with decomposition of the complexes takes place. The free ligands L have been isolated in 75–95% yields. The reaction of Me_3NO with $Fe(CO)_5$ in the presence of bidentate diene ligands L yielded substituted complexes $[LFe(CO)_3]$:[112]

$$Fe(CO)_5 + Me_3NO + L \rightarrow [LFe(CO)_3] + Me_3N + CO_2 + CO.$$

Since then the reactions involving decarbonylation by amine oxides have been used for preparative purposes.

In the interaction of $Fe(CO)_5$ with a twofold excess of Me_3NO in THF at −30 °C, evolution of CO_2 was observed; the complex $Fe(CO)_4(NMe_3)$ was obtained from the reaction mixture in 45% yield;[113] a mechanism for the oxidative decarbonylation, involving nucleophilic attack by Me_3NO on the carbon atom of the carbonyl ligand, has been proposed on the basis of the results:[107,113]

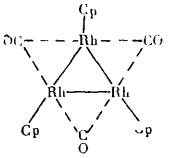


Many instances of oxidative decarbonylation reactions using amine oxides, some of which have been published in a review,[106] are known at present in the literature. It has been noted[107] that these reactions can be carried out in a wide range of solvents such as benzene, dichloromethane, chloroform, THF, acetonitrile, acetone, 2-methoxyethanol, and methanol.

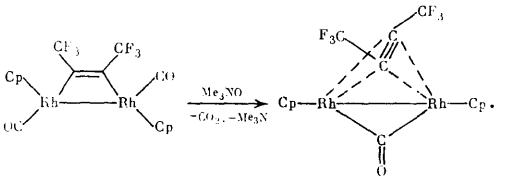
We shall present certain examples of the reactions involving the selective oxidation of CO in metal carbonyls. The interaction of $[W(CO)_5(PPh_3)]$ with Me_3NO in dichloromethane in the presence of SMe_2 led to the formation of $[W(CO)_4(PPh_3).(SMe_2)]$.[114] The reaction of $[Ru(CO)_2Cl_2bipy]$ (bipy = 2,2′-bipyridyl) with Me_3NO in molar proportions of 1 : 5 in pyridine formed the monosubstitution product $[Ru(CO)PyCl_2.bipy]$.[115] The authors of the above study point out that the attempts at the complete decarbonylation of $[Ru(CO)_2.Cl_2bipy]$ were unsuccessful. Refluxing of the homodinuclear complex $[Mn_2H(CN)(CO)_5Dppm]$ with an excess of $Me_3NO.2H_2O$ in a dichloromethane–methanol mixture for 88 h leads to the formation of the complex $[Mn_2H(CN)(CO)_4Dppm]$ in 24% yield; irradiation of the reaction mixture with visible light increases the rate of reaction and the yield of the final product.[116] Data on the oxidative decarbonylation of cluster compounds may be found in a number of publications.[107,117–124]

If the oxidative decarbonylation is carried out in the presence of electron-donating solvents, the reaction can influence the formation of solvato-complexes. For example, the removal of a carbonyl group from the triosmium cluster $Os_3(CO)_{12}$ with the aid of trimethylamine oxide in the presence of acetonitrile leads to the formation of the monosolvate $Os_3(CO)_{11}(MeCN)$. The reaction of $Os_3(CO)_{11}(MeCN)$ with yet another mole of Me_3NO gives rise to a high yield of $Os_3(CO)_{10}(MeCN)_2$.[119,120] The reaction does not proceed further and the trisolvate is not formed. According to the authors, this can be explained by the mutual influence of the ligands, which reduces the tendency of the carbonyl centres to undergo nucleophilic attack.

In the absence of an electron-donating ligand (or an electron-donating solvent) the coordination-unsaturated species formed as a result of the removal of CO can react with the initial compound to form a metal–metal bond.[125] Thus the interaction of Me_3NO with $CpRH(CO)_2$ in benzene leads to the formation of the trimer as the dominant product:

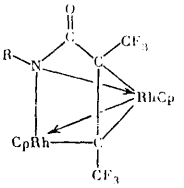


The decarbonylation of the complex $(\eta\text{-}Cp)_2Rh_2(CO)_2.(CF_3C_2CF_3)$ by trimethylamine oxide in dry acetone is accompanied by the rotation of the coordinated alkyne by 90° and the remaining coordinated carbonyl occupies a bridging position:[126–128]



The interaction of $Ru_2(CO)_6(DAB)$ (DAB = 1,4-substituted 1,4-diazabuta-1,3-diene) with trimethylamine oxide in a mixture of non-electron-donating solvents (dichloromethane and toluene) leads to the formation of the compound $Ru_2.(CO)_5(DAB)$.[129] The reaction alters the type of binding of the DAB ligand: instead of the 6e-(σ-N, μ^2-N′, η^2-C=N′) coordination, we have the coordination 8e(σ-N, σ-N′, η^2-C=N, η^2-C′=N′).

Many chemical properties of inner-sphere organic isocyanides are known to resemble those of coordinated carbon monoxide.[130] In a recently published study,[131] trimethylamine oxide was used to oxidise the isocyanide ligand RNC (R = Me, Bu, Pr, C_6H_{11}) coordinated to a rhodium atom in the complex $[(\eta^5\text{-}Cp)_2Rh_2(CO)(CNR)(CF_3C_2CF_3)]$. The oxygen is then transferred from Me_3NO to the isocyanide with formation of the isocyanate RNCO. The subsequent intramolecular rearrangement and evolution of CO results in the formation of a compound which has the following structure according to X-ray diffraction data:



VIII. OTHER OXIDANTS

Among other oxidants, mention should be made of the higher halides of Group V elements. Thus the oxidative halogenation of the complex $[Mo(\mu\text{-}C_8Me_8)Cp_2]$ by the mild oxidants $[NPr_4](SbCb_6)$ or $[PhCO](SbCl_6)$ in dichloromethane leads to the formation of the complex $[Mo(\mu\text{-}C_8Me_8).(\mu\text{-}Cl)Cp_2](SbCl_4)$ in a quantitative yield.[132] The authors[132]

suggest that the final product is obtained as a result of oxidation which is followed by the halogenation of the cation formed.

In order to obtain complexes with a coordinated SO_2 molecule, AsF_5 is widely used.[133-135] Thus the reaction of metallic zinc or cadmium with an excess of arsenic pentafluoride in liquid SO_2 leads to the formation of homogeneous solvato-complexes:[134,135]

$$M + 3AsF_5 \xrightarrow{SO_2} [M(SO_2)_2](AsF_6)_2 + AsF_3.$$

The complexes $[M(SO_2)_2(AsF_6)_2]_n$ have been obtained by the interaction of the metal M (M = Mn, Fe, Co, Ni, Cu, Zn, or Mg) and AsF_5 in molar proportions of 1:5 in liquid SO_2.[133]

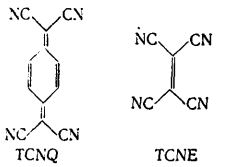
Organic 1,2-dihalides can oxidise certain metals. For example, the slow addition of Sm or Yb to a solution of 1,2-diiodoethane in THF leads to the formation of SmI_2 and YbI_2 in quantitative yields:[136]

$$M + ICH_2CH_2I \xrightarrow{THF} MI_2 + CH_2CH_2.$$

The reaction is rapid at room temperature.

A mixture of $AlCl_3$ and CH_2Cl_2 exhibits fairly strong oxidising properties.[137-139] Unfortunately the authors did not consider the oxidation mechanism and did not identify the reduction products. $AlCl_3$ in dichloromethane has been used to oxidise the molybdenum complex $[Mo(CO)_2(bipy)_2]$. After the completion of the reaction, the product was precipitated in the form of the dimer $[Mo(CO)_2(bipy)_2]_2 \cdot (BF_4)_2$ by adding $NaBF_4$ to the reaction mixture.[140]

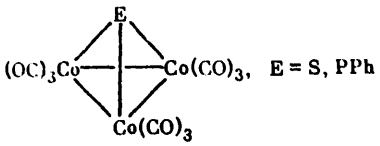
Tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE)



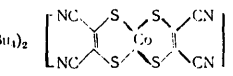
TCNQ

TCNE

are known to be fairly strong electron acceptors.[141,142] Stable radical-anions $TCNQ^-$ and $TCNE^-$ are formed in one-electron reduction. The half-wave potentials of the polarographic reduction of these compounds in acetonitrile (0.127 V for TCNQ and 0.152 V for TCNE) show that they are mild oxidants in the given solvents.[142] It has been established in a recently published study[143] that the clusters



react with TCNQ in ethanol, acetone, dichloroethane, THF, or dichloromethane to form the one-electron oxidation product $[ECo_3(CO)_9]^+$. TCNE oxidises the complex



with formation of the dimeric compound $[NBu_4)_2 \cdot [Co(C_4N_2S_2)_2]_2$.[144]

Organic disulphides can oxidise metal carbonyls in a photochemical reaction in accordance with the equation

$$[CpM(CO)_n]_2 + S_2R_2 \xrightarrow{h\nu} 2[CpM(CO)_n SR];$$

M = Fe, R = Me, n = 2 (Ref.145);

M = Ru, R = Me, Ph, Bz, n = 2 (Ref.146);

M = W, R = $Me_2NC(S)$, n = 3 (Ref.147).

The mechanism of processes of this kind involves the formation of extremely reactive metal carbonyl radicals as a result of photolysis, which are oxidised in a dark reaction by the organic disulphide with formation of thiolate complexes.[147]

In conclusion, one should note that many oxidants can be used in both aqueous and non-aqueous solutions. Thus instances of the employment of PbO_2 in a mixture of MeCN and CF_3CO_2H,[148] of Cp_2Fe^+ in acetonitrile[149,150] and THF,[151-153] of $Pb(OAc)_4$ in dichloromethane,[154] of $TiCl_3$ in dichloromethane,[155,156] etc. are known. The procedure involving the modification of "traditional" oxidants in order to impart hydrophobic properties to the latter is of interest. For example, the pyridine analogue of potassium dichromate, namely $(PyH)_2Cr_2O_7$, has been synthesised.[157] This compound is highly soluble in dimethylformamide, diethylacetamide, and dimethyl sulphoxide and is sparingly soluble in dichloromethane and chloroform. An analogue of hydrogen peroxide, namely the compound $(Me_4N)_2O_2$, is used to synthesise complexes in acetonitrile.[158]

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