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The Basicity of Transition Metal Complexes in Reactions with Aprotic Acids

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Data for the interaction of transition metal complexes (TMC) with aprotic acids, in which the TMC play the role of bases, are examined and reactions, in which the centre of the basicity of the TMC is the transition metal atom, and the ligands are discussed. The influence on the basicity of the central atom of its position in the Periodic System and of its ligand environment as well as the influence of the structure of the complex and the nature of the aprotic acid and the medium on the formation of donor-acceptor complexes between TMC and electron acceptors are considered. A systematic account is given of data for the interaction of TMC with various classes of acceptors: metal and non-metal halides, halogens, alkyl halides, metal cations, π-acids, and one-electron oxidants.
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I. INTRODUCTION

It is well known that many transition metal complexes (TMC) have nucleophilic properties and can play the role of bases in an acid–base interaction. The metal in such complexes is in a low oxidation state and can be attacked by various electrophiles. The basic properties of TMC were demonstrated for the first time in 1955 when the reversible protonation of π-complexes at the transition metal atom was discovered[1]. Studies in this field subsequently developed greatly and the infrared spectroscopic and NMR methods played a decisive role in the study of protonation[2-6].

The study of protonation yielded important data on the basicity of the metal atom and complexes, since the basicity of the central metal atom can be inferred qualitatively from the ease of protonation. In particular, a relation has been established between the ease of protonation and the position of the metal in the Periodic System. In series of isostructural compounds with the same ligands, differing only in the central transition metal atom, the basicity of the latter increases with increase of its atomic number within the limits of a single Group. In this sense, transition metal compounds differ sharply from bases containing elements of the main groups of the Periodic System, whose basicity diminishes on passing to heavier atoms within the limits of the same Group. The reason for this is in the difference between the properties of the orbitals involved in the formation of the donor–acceptor bonds. For main Group elements, the lone pair of n electrons of the sp^2- or sp^3-hybridised heteroatoms is involved in the interaction, i.e. the corresponding compounds are n-bases. For TMC, the highest occupied molecular orbital is a virtually pure d orbital of the metal and is occupied by d electrons, i.e. these complexes behave as d-bases.

The basic properties of TMC are shown not only in protonation reactions but also in reactions with many aprotic acids. The basicity of TMC can be shown in two aspects of their reactivity: (a) the interaction with an acceptor suitable as regards the symmetry and energy of the vacant orbital, leading to the formation of a new donor–acceptor chemical bond; (b) oxidation of the TMC involving the abstraction of one electron from the highest occupied molecular orbital without the formation of a new chemical bond. Such oxidation can proceed both chemically under the influence of a suitable oxidant (Ag^+, NO^+) and electrochemically. The study of these reactions greatly extends the scope of research into the basicity of TMC. These data are also important for the understanding of the mechanisms of many reactions of TMC, for example, reactions in the presence of Lewis acids and oxidative addition reactions.

In the present review an attempt is made to achieve a systematic arrangement of the extensive experimental data, which are available for the interaction with aprotic acids, from the standpoint of the basicity of the TMC. In this case we understand by basicity the ability of the TMC to form donor–acceptor (D–A) complexes (adducts) with electron acceptors involving an increase of the coordination number (C.N.) of the donor atoms. The possibility of the formation of an adduct depends not only on the properties of the donor molecules but also on the type of acceptor used. The strength of the D–A bond is determined by the relative energies and symmetries of the D and A orbitals involved in the formation of the bond and also by steric factors. The properties of the same TMC as a base can therefore be different in relation to different acceptors. The interactions of TMC with the following classes of electron acceptors have been considered: aprotic acids—metal and non-metal halides; halogens and alkyl halides; metal cations; π-acids; one-electron oxidants.

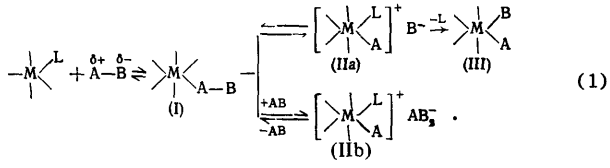
There are several possible basicity centres in the molecules of the TMC considered to which attack by the electrophile can be directed: the central metal atom, the O, S, or N atoms or ligands such as CO, CS, NO, N_2 or CN, halogen ligands, and finally π-ligands. It is shown below that the reactions with aprotic acids can lead to the formation of adducts not only via the metal atom but also via the ligand and that, depending on the type of complex, the aprotic acid, and the reaction conditions, the complexes can behave as d-bases, n-bases, or π-bases. Sometimes these possibilities are realised simultaneously.

A number of reviews devoted to the basicity of transition metal complexes have already been published, but some of these[6,7] cover only the literature up to 1970 and one[8] is concerned mainly with the basicity of carbonyl ligands and is incomplete.

Reactions via the central metal atom and via the ligand will be considered separately below.

II. INTERACTION VIA THE METAL ATOM

For five-ccordinate and six-coordinate complexes, the reactions via the metal atom can be represented by the following mechanism, where A–B is a conventional representation of a molecule of the Lewis acid:



(1)

The electron acceptor can add to the metal to give a neutral adduct (I), which can then be converted into an ionic compound (IIa) or (IIb) with dissociation of the A–B bond. The latter compounds should be electrically conducting in solutions. However, in the majority of cases the structure of the adduct cannot be establsihed exactly in solution, since conductimetric data are not always reliable or are not available. Owing to the reversibility of the formation reactions of compounds (I) and (II), an equilibrium is established in the solution as a result of which the observed conductivities can be low.

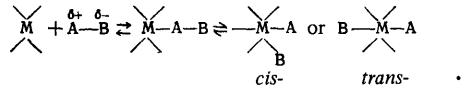
Adducts with two or several molecules of the Lewis acid frequently contain involved complex anions (for example, $SnCl_5^-$, $HgCl_3^-$, $Hg_2Cl_5^-$, etc.). The structure of the adduct in solution and in the crystal can be various. Thus polar solvents promote the conversion of adducts of type (I) into compounds of type (II).

The structure of complexes with Lewis acids has not always been established with sufficient reliability. For solid adducts, X-ray diffraction data are available in many instances, but the evidence for the structure has usually been reached solely on the basis of spectroscopic data. The equilibrium between the adduct and the initial compounds in solutions has been studied even less. The equilibrium position can be inferred, at least qualitatively, from such data for the relative basicities of the complexes. In other cases, the relative basicities of series of complexes can be established in accordance with the occurrence or non-occurrence of an interaction with a standard Lewis acid under identical conditions.

In the absence of structural data, the main criterion of the formation of adducts via the metal is provided by spectroscopic measurements. Complexes containing the CO ligand have been most widely investigated, because the CO stretching vibration frequencies are extremely sensitive to changes in the formal oxidation state of the metal. The interaction of the acceptor molecule with the central metal atom leads to an increase of the stretching vibration frequencies of the CO groups, which is associated with the decrease of the electron density at the metal atom and this entails a weakening of the $d_\pi(M) \rightarrow p_{\pi^*}(CO)$ dative bonds and an increase of the CO bond orders in the complex $\overline{M}-C\equiv\overset{+}{O}\leftrightarrows M=C=\ddot{O}:$. As in protonation involving the metal atom, such a frequency shift is believed to be a characteristic feature of the involvement of the metal atom in coordination to the Lewis acid. As will be shown below, other types of coordination of the acceptor lead to quite different changes in the spectra. It is not always possible to state with confidence which type of adduct has been obtained—(I) or (II). It is usually assumed that, in the formation of type (II) adducts, the formal positive charge on the metal atom increases by unity and the CO frequency shift should be the same as in protonation (100–150 cm^{-1}).

The electron density on the metal atom in adduct (I) should also be reduced but to a smaller extent; consequently the observed hypsochromic shift should be smaller. For example, complexes of the type $L_2Fe(CO)_2$ form 1:1 or 1:2 adducts with $HgCl_2$. The ν(CO) frequency shift is 70–80 cm^{-1} for the first type and 100–120 cm^{-1} for the second. Accordingly, the structures $L_2(CO)_3Fe \rightarrow HgCl_2$ and $[L_2(CO)_3FeHgCl]^+HgCl_3^-$ have been attributed to these adducts[9], which has been confirmed by conductimetric measurements.

The final product (III) of reaction (1) is formed by the elimination of a neutral ligand molecule, usually CO (the so-called oxidative elimination). This stage of the reaction is irreversible. In the present review reactions of this type will not be considered in detail (see the previous reviews[10,11]). In the case of tetracoordinate complexes reactions can proceed without the elimination of ligands, involving an expansion of the coordination sphere and an increase of the coordination number by two (oxidative addition reactions):



(2)

We may note that the basicity of the central metal atom is one of the main factors which determine the course of such reactions. This can be seen from the following reaction as an example[12]:

$$(bipy)M(CO)_4 + 2HgCl_2 \rightleftharpoons (bipy)M(CO)_4 \cdot 2HgCl_2 \xrightarrow{-CO} (bipy)M(CO)_3Cl(HgCl) + HgCl_2$$

(M = Mo or W; bipy = 2,2'-bipyridyl).

For M = W, it is possible to isolate an unstable intermediate adduct $(bipy)W(CO)_4.2HgX_2$ (X = Cl or Br), which rapidly evolves CO and gives rise to the stable tricarbonyl derivative $(bipy)W(CO)_3X(HgX)$. For the corresponding molybdenum complex, the intermediate adduct is so unstable that one obtains immediately the tricarbonyl derivative $(bipy)Mo(CO)_3X(HgX)$. The reaction with $SnCl_4$ yields in both cases the oxidative addition product $(bipy)M(CO)_3.Cl(SnCl_3)$, where M = Mo or W.[12,13]

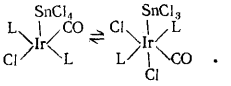
The interaction of phosphine derivatives $(diphos)M(CO)_4$ (diphos = $Ph_2PCH_2CH_2PPh_2$) with $HgCl_2$ proceeds without the evolution of CO and the adducts $(diphos)M(CO)_4.HgCl_2$ are formed[12]. The infrared spectra of these adducts in solution contain the ν(CO) bands of the initial complexes and in addition higher-frequency bands, corresponding to an increase of the oxidation state of the metal atom, appear, i.e. the adducts are in equilibrium with the initial substances in solution. The conductances Λ_M of solutions of the adducts in acetonitrile are low, but the addition of an excess of $HgCl_2$ lowers the degree of dissociation of the adduct and increases Λ_M. On this basis, it is postulated that the adducts have the structure $[(diphos)M(CO)_4.HgCl]^+Cl^-$.

It is seen from the examples presented that, depending on the nature of the reactants, reaction (1) can give rise to different products.

The interaction with aprotic acids is extremely characteristic of square planar rhodium and iridium complexes. Here there is a possibility of a donor–acceptor adduct (C.N. = 5

for M) or of oxidative addition (C,N. = 6).[6,14] For example, *trans*-$L_2Ir(CO)Cl$ ($L = PPh_3$) reacts with HgX_2 to give the oxidative addition products $L_2(CO)ClIr\begin{matrix}\nearrow X\\ \searrow HgX\end{matrix}$.[15] The same complex forms 1:1 and 1:2 adducts with BF_3 in solution. The 1:1 adduct[16] is a simple adduct with an Ir–B donor-acceptor bond whose (CO) frequency has been increased by 100 cm^{-1} compared with the carbonyl frequency of the initial complex. For the 1:2 adduct, ν(CO) does not differ appreciably from the value for the 1:1 adduct. The structure of the 1:2 adduct is obscure. It has been suggested that its second BF_3 molecule is not linked to the Ir atom but is connected to the first BF_3 group via a bridge of fluorine atoms[5].

The reaction of *trans*-$L_2Ir(CO)Cl$ with $SnCl_4$, leading to the formation of $L_2(CO)ClIr.SnCl_4$, is extremely interesting[17]. The resulting complex is monomeric and non-conducting. The infrared spectrum shows two bands in the carbonyl region, at 2080 and 2020 cm^{-1} in the solid state and at 2080 and 2041 cm^{-1} in chloroform. The presence of the two ν(CO) bands can be explained by the presence of isomers which undergo a rapid interconversion:



This is an unusual type of isomerism involving a change in the formal oxidation state of the central metal atom. The higher-frequency band corresponds to the oxidative addition product and the lower-frequency band is associated with the donor–acceptor adduct.

Thus the acid–base interaction of the metal atom in the complex L_nM with the aprotic acid AB can lead to several types of compounds: neutral adducts $L_nM \rightarrow AB$ and salt-like compounds $[L_nM-A]^+B^-$ or $[L_nM-A]^+AB_2^-$. The mode of reaction depends on a number of factors: the nature of the metal, the nature of the ligands surrounding it, the type of Lewis acid, and the solvent. Although the available data are non-systematic, they nevertheless make it possible to trace a number of regularities.

1. The Influence of the Nature of the Central Metal Atom

The dependence of the basicity of the complex on the nature of the central metal atom can be established by comparing the behaviour of complexes differing solely by the central atom in reactions with the same electron acceptor.

It was already noted above that, on treatment with BF_3, the complex $L_2Ir(CO)Cl$ ($L = PPh_3$) forms adducts via the metal atom, which contain the $Ir \rightarrow B$ bond.[16] The analogous rhodium complex $L_2Rh(CO)Cl$ does not form adducts with BF_3, which leads to the conclusion that the Ir atom is more basic than the Rh atom. In contrast to the rhodium complex, the iridium complex is also capable of forming a compound with O_2.[14] Thus, atoms with a higher atomic number proved to be more basic in the given Group of the Periodic System. This behaviour, which agrees with that found in the study of protonation[3–5,18–21], is extremely general; it holds also in other Groups of the Periodic System.

Thus cyclopentadienyltricarbonylmanganese $CpMn(CO)_3$ (CTM) does not interact with $TiCl_4$, while the addition of $TiCl_4$ to the corresponding rhenium complex $CpRe(CO)_3$ (CTR) in CH_2Cl_2 gives rise to a spectrum, where, apart from the ν(CO) bands of the initial substance, there are also bands of the adducts displaced towards higher wavenumbers by more than 100 cm^{-1},[22] which is characteristic of adducts formed via the metal atom.

After the addition of an excess of $SnCl_4$ in CH_2Cl_2, the infrared spectrum of the phosphite derivative of CTM, i.e. $CpMn(CO)_2P(OPh)_3$, contains the ν(CO) frequencies of both the initial complex and the adduct[23]. For $CpRe(CO)_2P(OPh)_3$ under the same conditions, the equilibrium is almost wholly displaced towards the formation of the adduct[22]. These data indicate more pronounced basic properties of rhenium compared with manganese.

The arene complexes of Group VI transition metals behave similarly. Thus $MsCr(CO)_3$ (Ms = mesitylene) is in equilibrium with the addition product in CH_2Cl_2 in the presence of an excess of $SnCl_4$. The equilibrium involving the corresponding Mo and W compounds is wholly displaced towards the adduct. Analysis of the available data shows[22] that the basicity of the metal increases in the sequence Cr < Mo < W. An analogous conclusion was reached for the triad Co < Rh < Ir.[14,24]

2. The Influence of the Ligand Environment on the Basicity of the Metal in the Complex

The basicity of the transition metal atom in the complex depends very markedly on the nature of the surrounding ligands. The replacement of ligands by species with more marked electron-donating properties, for example, tertiary phosphines, leads to an increase of basicity and, conversely, the introduction of electron-accepting ligands suppresses basicity.

CTM does not interact with $SnCl_4$ in solutions[23], but the addition of five electron-donating ethyl groups in the Cp ring enables the complex $(Et_5C_5)Mn(CO)_3$ to form an adduct with $SnCl_4$ in solution, although the equilibrium is in this case displaced towards the formation of the initial substances. The replacement of one CO group by a phosphine ligand PR_3, with more pronounced electron-donating properties, increases the basicity of the Mn atom to an even greater extent. The basicity then depends on the electron-donating properties of the group R in the ligand PR_3, increasing sharply in the sequence OPh ≪ Ph < alkyl. Like CTM, CTR does not interact with $SnCl_4$, but the replacement of CO by PR_3 sharply increases the basicity and makes the complex capable of forming adducts; the reaction proceeds readily in solution and goes almost to completion[22].

The complex $MsCr(CO)_3$ (Ms = mesitylene) is in equilibrium with the adduct molecules in the presence of an excess of $SnCl_4$. The phosphine derivative $MsCr(CO)_2PPh_3$ is almost completely converted into an adduct in the presence of an excess of $SnCl_4$.[22]

The substitution of two CO groups in $CpMn(CO)_3$ by two phosphine ligands is accompanied by an even greater increase of the basicity of the manganese atom. Diphosphine complexes of the type $CpMn(CO)L_2$ [$L_2 = (PPh_3)_2$ or the bidentate diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1–3$)] react in solution not only with $SnCl_4$ but also with weaker aprotic acids $SbCl_3$, $HgCl_2$, and $GeCl_4$.[23] In all cases the single ν(CO) frequency then increases by 100–110 cm^{-1} and, depending on the ratio of the amounts of the initial reactants, the spectrum contains the bands of both forms or only of the adducts. In the presence of an excess of $SnCl_4$, $SbCl_3$, or $HgCl_2$ only the bands of the adducts were observed in the infrared spectrum of the solution. For $GeCl_4$, both bands were observed even when the compound was present in a large excess in solution, and their intensity ratio indicates a shift of the equilibrium towards the initial compound.

3. Dependence of the Nature of the Interaction on the Aprotic Acid

The mode of reaction of TMC in many respects depends on the type of acceptor molecule. Certain Lewis acids are capable of interacting with complexes not only via the metal atom but also via the ligands. These instances will be examined separately below. This section deals solely with interactions via the metal.

The higher the basicity of the metal atom in the complex, the greater the range of aprotic acids with which it can interact. Thus $(Ph_3P)_2Rh(CO)Cl$ does not interact with BF_3 but does so with BCl_3 and BBr_3, the adduct with BBr_3 being most stable[25,26], which agrees with the usual sequence based on the variation of the Lewis acidity: $BF_3 < BCl_3 < BBr_3$.[27] The complex $CpMn(CO)_2PPh_3$ forms adducts with $SnCl_4$, but does not react with the weaker aprotic acids $GeCl_4$ and $SbCl_3$. The complexes $CpMn(CO)L_2$, where $L_2 = (Ph_3P)_2$ or bidentate diphosphine ligands, form adducts with weak Lewis acids, and the latter can be arranged in the following sequence in terms of the ease of interaction: $SnCl_4 \gg SbCl_3 \cong HgCl_2 > GeCl_4$.[23] The sequence $TiCl_4 > SnCl_4 > SnBr_4$ has been established for $CpRe(CO)_2L$.[22]

$AlCl_3$, which is capable of forming adducts via both the metal and the ligands (see below), occupies a special place among Lewis acids.

III. INTERACTION OF LEWIS ACIDS WITH TRANSITION METAL COMPLEXES VIA THE LIGANDS

Another type of interaction of Lewis acids with TMC involves the formation of adducts with participation of the lone electron pair of one of the ligand atoms. This can be the oxygen atom in the CO and NO groups, the sulphur atom in CS, the nitrogen atom in the N_2 and CN ligands, and a halogen atom.

For complexes containing halogen or nitrile ligands at the transition metal atom, the reaction with Lewis acids proceeds as a rule via an *n*-electron pair of the ligand. If the complex contains, together with halogen or nitrile ligands, carbonyl or nitrosyl ligands, then the shift of the vibration frequencies of the latter can be a sign of the formation of donor–acceptor adducts. The coordination of Lewis acids (A) to halogen or nitrile ligands (X) ($O\equiv C-\widetilde{M}-\widetilde{X}:\rightarrow A$) leads to a slight increase of the ν(CO) or ν(NO) frequency—by 15–25 cm^{-1}. Such interaction entails a weakening of the M–CO dative bonds and correspondingly, within the framework of the mechanism $M^--C\equiv O^{+}\leftrightarrow M=C=O$, an increase of the CO bond orders. However, this influence of the acceptor is significantly weaker than in the direct interaction with the metal atom: $O\equiv C-\widetilde{M}\rightarrow A$ [$\Delta\nu$(CO) ≅ 100–150 cm^{-1}. As an example[28] one can quote the ν(CO) frequencies (cm^{-1}) in the spectra of the complexes $CpRe(CO)_2Br_2$ (2005, 2068), $CpRe(CO)_2Br(Br\rightarrow AlCl_3)$ (2022, 2083), and $CpRe(CO)_2$. $.Br(Br\rightarrow AlCl_3)$ (2022, 2083), and $CpRe(CO)_2(Br\rightarrow AlCl_3)_2$ (2031, 2096).

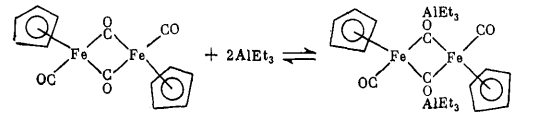
The donor–acceptor interaction of Lewis acids with the CN group leads to an increase of the stretching vibration frequency of the latter. The CN group behaves analogously in any nitrile and not only in transition metal complexes. It is believed that the increase of the ν(CN) frequency on coordination is associated with the increase of the force constant of the CN bond and with the change in the mechanism of the vibrations of the molecule when it is bound in a complex[29–31].

When the complex $CpFe(CO)_2(CN)$ is coordinated to Lewis acids ER_3 (E = Al or Ga; R = Me or Cl) or BX_3 (X = H, F, Cl, Br, or Me), the stretching vibration frequencies of all three groups (two CO groups and one CN group) increase[32]. The frequency shifts (Table 1) lead to the conclusion that the acceptor is coordinated to the CN group.

Table 1. The stretching vibration frequencies of the CN and CO groups in the adducts of $CpFe(CO)_2(CN)$ with Lewis acids.

Complex	ν_{CN}, cm^{-1}	ν_{CO}, cm^{-1}
$CpFe(CO)_2(CN)$	2120	2055 2007
$CpFe(CO)_2(CN\rightarrow AlCl_3)$	2168	2068 2026
$CpFe(CO)_2(CN\rightarrow BF_3)$	2201	2073 2031

The interaction of the complex with the carbonyl ligand is characteristic of the strongest Lewis acids—boron and aluminium derivatives. The possibility of the addition of a Lewis acid to the oxygen atom of the carbonyl ligand in the complex was first observed for bridging CO groups in the dimeric complex $[CpFe(CO)_2]_2$, which forms an adduct with two $AlEt_3$ molecules[33,34]:



The structure of the adduct was established by X-ray diffraction[33]. Its formation leads to an appreciable decrease of the ν(CO) frequencies of the bridging groups involved in the interaction with aluminium and to an increase of the stretching vibration frequencies of the terminal carbonyl ligands. The decrease of the stretching vibration frequencies of the CO groups linked to aluminium is caused by the weakening of the CO bonds owing to the shift of electron density towards the acceptor molecule. This entails a strengthening of the $M\rightarrow C$ dative bonds in the $MCO\rightarrow Al$ fragments and their weakening for the CO groups not coordinated to aluminium, which leads in its turn to an increase of the terminal CO bond orders and an increase of their vibration frequencies.

The study of the interaction of complexes containing both bridging and terminal CO groups with Lewis acids derived from aluminium showed that the bridging carbonyl groups are more basic and that the basicity of the oxygen atom in the CO groups increases in the following sequence: terminal groups < double bridge groups < triple bridge groups[8]. The difference between the basicity of the bridging and terminal CO groups can be used to displace the equilibrium and to convert terminal groups into bridging groups, for example[35,36]:

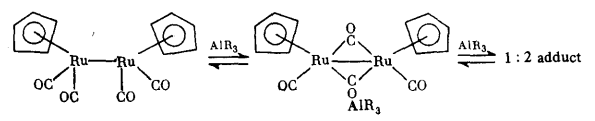
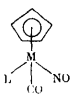
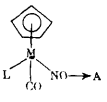
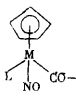
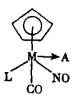
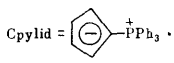


Table 2. The stretching vibration frequencies of the CO and NO groups (cm^{-1}, in CH_2Cl_2) of the complexes $CpM(CO)_2NO$ and $CpM(CO)(NO)PPh_3$ (M = Mo or W) and their adducts with Lewis acids[22].

Complex								
	ν(NO)	ν(CO)	ν(NO)	ν(CO)	ν(NO)	ν(CO)	ν(NO)	ν(CO)
$CpMo(CO)_2NO$	1670 s.	1942 s. 2021 s.	—	—	—	—	—	—
$CpMo(CO)_2NO+SnCl_4$	1670 s.	1945 s. 2020 s.	—	—	—	—	—	—
$CpMo(CO)_2NO+TiCl_4$	1666 s.	1941 s. 2020 s.	1486 m.	2003 sh. 2065 m.	—	—	—	—
$CpMo(CO)_2NO+AlCl_3$	1670 s.	1950 s. 2025 v.s.	1450 s.	2025 v.s. 2087 v.s.	1710 m.	1735 sh. 2065 m.		
$CpW(CO)_2NO$	1660 s.	1929 s. 2011 s.	—	—	—	—	—	—
$CpW(CO)_2NO+SnCl_4$	1658 s.	1929 s. 2011 v.s.	1481 m.	1981 m. 2051 m	—	—	—	—
$CpW(CO)_2NO+AlCl_3$	1655 s.	1930 s. 2010 v.s.	1450 s.	2010 v.s. 2055 s.	—	—	—	—
$CpMo(CO)(NO)PPh_3$	1606 s.	1941 s.	—	—	—	—	—	—
$CpMo(CO)(NO)PPh_3+SnCl_4$	—		—	—	—	—	1747 s.	2070 s.
$CpMo(CO)(NO)PPh_3+AlCl_3$	—		1390 s.	1991 s.	—	—	1722 s.	2070 s.
$CpW(CO)(NO)PPh_3$	1595 s.	1900 s.	—	—	—	—	—	—
$CpW(CO)(NO)PPh_3+SnCl_4$	—	—	—	—	—	—	1740 s.	2050 s.
$CpW(CO)(NO)PPh_3+AlCl_3$	1590 m.	1900 m.	1400 s.	1975 s.	—	—	1713 m.	2070 m.

Note. v.s = very strong (intense), s = strong, m = medium, and sh = shoulder.

Interaction with CO, N_2, and NO terminal ligands leads, as for the coordination with bridging CO groups, to a significant decrease of the stretching vibration frequency of the coordinated group and to an increase of the stretching vibration frequencies of ligands not linked to the aprotic acid. For example[37], the ν(CO) frequencies are 1904, 1808, and 1791 cm^{-1} for $CpylidMo(CO)_3$ and 1932, 1845, and 1665 cm^{-1} for $CpylidMo(CO)_2(CO \rightarrow AlMe_3)$:



The same transition metal complexes with different Lewis acids can react in different ways—either via the metal atom or via the ligands (CO, NO). For example, $CpylidMo(CO)_3$ interacts with H^+, BF_3, $TiCl_4$, and $AlCl_3$ via the Mo atom and with $AlMe_3$ via the CO group[19,22,37].

The simultaneous formation in solution of adducts both via the metal atom and via the terminal CO or NO groups has been observed in some cases. Section IV deals in detail with factors influencing the mode of reaction in competitive coordination.

IV. COMPETITIVE COORDINATION

As shown above, transition metal complexes can react with aprotic acids to form adducts via both the metal and via the ligands. The mode of reaction depends on the relative basicities of the metal atom and the lone electron pairs of the ligands and on the nature of the acceptor and the solvent. Depending on these factors, the same complex can interact differently with different Lewis acids and sometimes there is a possibility of the simultaneous formation of adducts of different types.

This is clearly seen from the example of the complexes $CpM(CO)_2(NO)$ and $CpM(CO)(NO)(PPh_3)$ (M = Mo or W).[22] They are capable of forming three different types of adducts: via the metal and via the oxygen atoms of the carbonyl or nitrosyl ligand. The most basic centre in the $CpM(CO)_2(NO)$ molecule is the nitrosyl oxygen atom. Thus the formation of adducts via the NO groups with complexes of the type Cp_3Ln, where Ln = lanthanide, has been described[38]. $TiCl_4$ and $SnCl_4$, which usually interact with *d*-bases and are coordinated to the metal atom, in this case also interact with the oxygen atom of the NO group[22]. Under these conditions, $SnCl_4$ does not interact with $CpMo(CO)_2(NO)$, but forms an adduct with $CpW(CO)_2(NO)$. The higher basicity of the nitrosyl oxygen atom in the tungsten derivative compared with the molybdenum compound is caused by the more marked shift of electron density from the W atom ($d_\pi - p_\pi$ interaction); an analogous conclusion follows from spectroscopic data[39].

The phosphine derivatives $CpM(CO)(NO)(PPh_3)$, in which the basicity of the M atom is greatly enhanced, form adducts with $SnCl_4$ via the metal atom. The differences between the reactions can be clearly followed on the basis of the infrared spectra. In the adducts via the NO group the ν(NO) frequencies are reduced by more than 200 cm^{-1} compared with the initial comlexes, while the ν(CO) frequencies are increased by 40–70 cm^{-1}. In the adducts formed via the metal atom, both ν(CO) and ν(NO) are displaced towards higher frequencies by ~150 cm^{-1} (Table 2). The increase of the basicity of the central atom after the introduction of the phosphine ligand makes complex formation via the metal atom energetically more favourable than coordination via the nitrosyl group.

The complex $CpW(CO)_2(NO)$ forms an adduct with $AlCl_3$ in CH_2Cl_2 via the oxygen atom of the NO ligand. The behaviour of the molybdenum compound $CpMo(CO)_2(NO)$ in relation to $AlCl_3$ is interesting. The somewhat reduced basicity of the nitrosyl oxygen atom, compared with the corresponding tungsten complex, leads to competition between the oxygen atoms of the carbonyl and nitrosyl groups, although here coordination via the nitrosyl group predominates (Table 1).

In the triphenylphosphine derivatives $CpM(CO)(NO)(PPh_3)$ (M = Mo or W) the basicity of the metal atom is increased, which leads to competition between the metal and the nitrosyl

oxygen atom in the reaction with $AlCl_3$. The tungsten complex forms adducts via both the nitrosyl group and the metal atom. Whereas coordination to the metal only is observed in the interaction with $SnCl_4$, in the interaction with $AlCl_3$ the formation of an adduct via the oxygen atom of the nitrosyl group predominates, which is indicated by the ratio of the intensities of the corresponding infrared bands (Table 2). The situation is similar for the molybdenum complex, but the content of the adduct formed via the metal atom is increased relative to the tungsten complex, which may be associated with a somewhat lower basicity of the nitrosyl oxygen atom in the molybdenum derivative.

Thus, depending on the relative basicities of the metal and the carbonyl and nitrosyl oxygen atom and also on the nature of the acceptor, there is a possibility of donor–acceptor interactions of different types for carbonyl nitrosyl complexes: with participation of the transition metal atom as the centre of basicity, with participation of the oxygen atom of the carbonyl or nitrosyl ligand, or with the simultaneous formation of both types of adducts.

The influence of the solvent on the nature of the donor–acceptor interaction has been observed in the study of the reaction of $CpMn(CO)_3$ with $AlCl_3$.[28] It has been shown by infrared spectroscopy that in benzene the Lewis acid is coordinated to the carbonyl group, while in CH_2Cl_2 an adduct is formed via the metal atom, i.e. $Cp(CO)_3Mn \rightarrow AlCl_3$, in addition to the adduct $CpMn(CO)_2.(CO \rightarrow AlCl_3)$. The introduction of donor ligands facilitates the interaction via the metal. In benzene the complex $CpMn(CO)_2(PPh)_3$ gives rise to a mixture of adducts via the oxygen atom of the CO group and via the manganese atom; in CH_2Cl_2 the formation of an adduct via the metal atom only was observed. Other complexes behave analogously in their reactions with $AlCl_3$ (see below). Examples of different types of reactions as a function of the acceptor are presented in Table 3.

Table 3. Dependence of the mode of coordination of the Lewis acid to the transition metal complex on the nature of the acid.

Transition metal complex base	Acceptor	
	bond with M atom	bond with ligand*
$(Ph_3P^+—C_5H_4^-)Mo(CO)_3$	H^+, BF_3, $TiCl_4$, $AlCl_3$	$AlMe_3$
$CpW(CO)_3^-$	H^+, $InPh_3$	$AlPh_3$, $MgPy_4^{2+}$, $Al(THF)_3^{3+}$
$CpM(CO)(NO)(PPh_3)$ (M = Mo, W)	$SnCl_4$, $AlCl_3$	$AlCl_3$
$CpRe(CO)_3$	$TiCl_4$, $AlCl_3$	$AlCl_3$
Arene $M(CO)_3$ (M = Cr, Mo, W)	H^+, $HgCl_2$, $TiCl_4$, $SnCl_4$, $AlCl_3$	$AlCl_3$
$[CpFe(CO)_2]_2$	H^+	AlR_3, BCl_3, BBr_3

*Py = pyridine.

On the other hand, the same Lewis acid can interact in different ways with the complex depending on its structure. Thus $SnCl_4$ is coordinated via the metal atom to the complexes $AreneM(CO)_3$† (M = Cr, Mo, or W), $CpM(CO)(NO)PPh_3$ (M = Mo or W), $CpM(CO)_2L$ (M = Mn or Re; L = PR_3), *trans*-$IrCl(CO)(PPh_3)_2$, and Cp_2Ru. However, one should note that the coordination of $CpW(CO)_2(NO)$ involves the nitrosyl oxygen atom and that of $CpCr(NO)_2Cl$ involves the chlorine atom. Compounds of the type AlR_3 form adducts via the metal atom with the complexes $CpM(CO)_nL_{3-n}$ (M = Mn, $n = 1–3$; M = Re, $n = 2, 3$; L = PR_3), $AreneM(CO)_3$ (M = Cr, Mo, or W), $(C_6H_6)Cr(CO)_2PPh_3$, $CpM(CO)_4$ (M = V or Nb), $CpV(CO)_3PPh_3$, $Fe(CO)_n(PPh_3)_{5-n}$ ($n = 3, 4$), CpReH, and Cp_2WH. In the case of $[CpFe(CO)_2]_2$ and a number of other complexes with bridging carbonyl ligands the coordination involves the oxygen atom of the bridging CO groups. The compounds $CpM(CO)_3$ (M = Mn or Re), $CpMn(CO)_2PPh_3$, $AreneM(CO)_3$ (M = Cr, Mo, or W), $CpV(CO)_n(PPh_3)_{4-n}$ ($n = 3, 4$), and $Mo(phen)(PPh_3)_2(CO)_2$ react with AlR_3 via the terminal CO groups, $CpM(CO)_n.(NO)L_{2-n}$ (M = Mo or W; $n = 1, 2$) are coordinated via the oxygen of the NO ligand, $CpRe(CO)_2Br_2$ and $CpCr(NO)_2Cl$ are coordinated via the halogen atom, and $CpFe(CO)_2CN$ is coordinated via the nitrogen atom of the cyano-group.

V. REACTIONS OF TRANSITION METAL COMPLEXES WITH ACCEPTORS OF DIFFERENT TYPES

1. Reactions with Derivatives of Group I–V Elements

(*a*) *Derivatives of Group I elements (Cu and Ag) as acceptors.* There are few examples of the interaction of TMC with acceptors derived from Group I elements. Thus $(diphos)_2.W(CO)(CS)$ reacts with $AgBF_4$ to form the product $\{[(diphos)_2W(CO)CS]_2Ag\}^+BF_4^-$, in which the acceptor is coordinated to the S atom of the CS ligand[40]. The compound $CpCoL_2$ interacts with $[L_2CuCl]_2$ via the metal atom, forming $CpL_2Co \rightarrow CuL_2Cl$ (L = PMe_3).[41]

(*b*) *Group II metal (Zn and Hg) halides.* Data for the interaction of EX_2 (E = Zn or Hg; X = halogen) with different complexes are presented in Table 4. There are no examples of coordination via the lone electron pairs of ligands such as CO, NO, N_2, CN or halogen for mercury or zinc derivatives, but coordination of HgX_2 to the sulphur atom of the CS ligand is known[40].

The Lewis acids HgX_2 are capable of forming adducts of different compositions (ranging from 1:1 to 1:7), and this behaviour is in fact extremely characteristic of these compounds. As mentioned above, 1:1 adducts can be either donor–acceptor complexes with $M \rightarrow HgX_2$ linkages or salts $[M–HgX]^+X^-$. In the solid state additional acceptor molecules sometimes occupy sites in the crystal lattice without forming a direct bond with the donor molecule but participating in intermolecular coordination. This is particularly characteristic of the adducts with HgX_2. For example, the crystal lattice of $Cp_2Ru.3HgCl_2$[42] contains the $Cp_2Ru \rightarrow HgCl_2$, $[Cp_2RuHgCl]^+Cl^-$, and $HgCl_2$ molecules.

X-Ray diffraction analysis of the complexes $CpCo(CO)_2.HgCl_2$[43,44] and $Cp_2Ru.HgX_2$ (X = Cl or Br)[45] indicates the formation of a metal–metal covalent bond. The Co → Hg bond length in the donor–acceptor adduct is 2.578 Å; the formation of this adduct increases ν(CO) by 75 cm^{-1}.[44,46] According to X-ray diffraction data, the 1:3 adduct has a CO–Hg bond with a length of 2.504 Å, i.e. shorter than in the 1:1 adduct. A crystal of the 1:3 complex contains the $[CpCo(CO)_2HgCl]^+$ cations, Cl^- anions, and two $HgCl_2$ molecules[47]. The formation of this complex causes a large shift of ν(CO) (by 90 cm^{-1}). The frequency shifts agree with the values quoted above for the adducts $L_2Fe(CO)_3.HgX_2$.[9]

†Here and henceforth Arene = η^6-C_6H_6 and its homologues (mesitylene and hexamethylbenzene).

Together with an intense ν(Cp–Ru)(symm.) line, yet another intense line appears in the Raman spectra of the adducts $Cp_2Ru.HgX_2$ (X = Cl or Br),[45] whose intensity does not change significantly on passing from the $HgCl_2$ adduct to the $HgBr_2$ adduct. This line (137 cm^{-1} for Cl and 130 cm^{-1} for Br) has been assigned to the vibration of the Ru–Hg bond. The Cp–Ru–Cp stretching vibration bands change slightly on coordination to a Lewis acid (by +5 cm^{-1}). The interaction of HgX_2 with Cp_2Ru has apparently little influence on the bonds between ruthenium and Cp rings, since the ruthenium atom uses non-bonding d electrons in the formation of a donor–acceptor bond with HgX_2.

Table 4. The interaction of transition metal complexes with Group II metal halides.

Initial substances	Compn. of adduct	Proposed structure	Refs.
$(Me_3C_6H_3)$ Cr $(CO)_3$ + $HgCl_2$	1:2	$(Me_3C_6H_3)$ Cr $(CO)_3 \cdot 2HgCl_2$	12
$(Me_3C_6H_3)$ Mo $(CO)_3$ + HgX_2 (X = Cl, Br)	1:1	$(Me_3C_6H_3)$ $(CO)_3Mo—HgX_2$	12
Ditto	1:2	$[(Me_3C_6H_3)$ $(CO)_3MoHgX]^+HgX_3^-$	12
(1, 3, 5-C_7H_8) Mo $(CO)_3$ + HgX_2 (X = Cl, Br)	1:1	(1, 3, 5-C_7H_8) $(CO)_3Mo—HgX_2$	12
(bipy) $W(CO_4$ + HgX_2 (X = Cl or Br; bipy = 2,2-bipyridyl)	1:2	bipy $(CO)_4W \cdot 2HgCl_2$	12
Ditto	--	bipy $(CO)_3WX$ (HgX)	12
(bipy) Mo $(CO)_4$ + HgX_2 (X = Cl, Br)	—	bipy $(CO)_3MoX$ (HgX)	12
(diphos) M $(CO)_4$ + HgX_2 (M = Mo, W; X = Cl, Br)		[(diphos) M $(CO)_4HgX]^+X^-$	12
$(diphos)_2M$ $(CO)_2$ + HgX_2 (M = Mo, W; X = Cl, Br, I)	1:2	$[(diphos)_2(CO)_2$ M $(HgX)]^+HgX_3^-$	12
(C_6H_6) Cr $(CO)_{3-n}L_n$(L = PPh_3, n = 0,1)	1:2; 1:3	—	51, 52
CpM $(CO)_2L$ + $HgCl_2$ (M = Mn, Re; L = PPh_3, $AsPh_3$, $SbPh_3$)	1:4—5	Cp $(CO)_2LMn \cdot nHgCl_2$	53
Fe $(CO)_5$ + $HgCl_2$	1:1; 1:2	—	54
Ditto	--	Fe $(CO)_4(HgCl)_2$	54
(PPh_3) Fe $(CO)_4$ + $HgCl_2$	1:2	—	12
$(EPh_3)_2$Fe $(CO)_3$ + HgX (E = P, As, Sb; X = Cl, Br)	1:1	$(EPh_3)_2(CO)_3—HgX_2$	55
[P $(OPh)_3]_2$Fe $(CO)_3$ + HgX_2 (X = Cl, Br)	1:2	$[P(OPh)_3]_2(CO)_3Fe—HgX_2$	55
Cp_2Fe + HgX_2 (X = Cl, Br)	1:7	red—adduct, blue—Cp_2Fe^+ salt	45
(RC_6H_4) Fe (C_6H_4R') + HgX_2	1:6—7	—	56
$(Ph_2PC_6H_4)_2$Fe + HgX_2 (X = Cl, Br)	1:1; 1:2	—	56
trans- $(PPh_3)_2$M (CO_3) + HgX_2 (M = Ru, Os; X = Cl, Br, I)	1:2	$[(PPh_3)_2$ M $(CO)_3(HgX)]^+$ HgX_3^-	57
Cp_2Ru + HgX_2(X = Cl, Br)	1:1*	$Cp_2Ru—HgBr_2$	45
Ditto	1:3*	$[Cp_2Ru—HgCl_2]$ $[Cp_2Ru—HgCl]^+$ Cl · $[HgCl_2]$	42
Cp_2Os + $HgCl_2$	1:2	$Cp_2Os—HgCl_2$	58
CpCo $(CO)_2$ + HgX_2(X = Cl, Br)	1:1*	Cp $(CO)_2Co—HgX_2$	43, 44, 46
Ditto	1:3*	[CpCo $(CO)_2(HgX)]^+$ X^- + $2HgX_2$	47
$CpCoL_2$ + $HgCl_2$(L = PMe_3)	1:1	$CpL_2Co—HgCl_2$	41
$CpCoL_2$ + $ZnCl_2$ + (L = PMe_3)	1:1	$CpL_2Co—ZnLCl_2$	41
CpIr (CO) (PPh_3) + $HgCl_2$	1:1	Cp (CO) (PPh_3) Ir—$HgCl_2$	59
CpIr (CO) (PPh_3) + $ZnBr_2$	1:1	Cp (CO) (PPh_3) Ir—$ZnBr_2$	59

*The structure of the reaction product was established by X-ray diffraction.

In contrast to ruthenocene, the interaction of ferrocene with mercury halides is more complex. Regardless of the reactant ratio, the same product, having the 1:7 composition, has been obtained for mercury(II) chloride[45]. A red precipitate is formed initially, turning blue on standing.

The red compound formed with $HgBr_2$ has not been isolated. The red compound $Cp_2Fe.7HgCl_2$ is diamagnetic at room temperature, while the blue compound is paramagnetic and has a magnetic moment close to that for ferrocenium salts. On heating, the red product becomes blue. On the basis of these data, it has been suggested that the red compound contains the Fe–Hg bond and is an adduct of Cp_2Fe with $HgCl_2$, while the blue compound consists of $CpFe^+$ and a complex anion. The above structure of the blue product is also supported by the finding that, after the addition of NH_4PF_6 to its aqueous solution, $[Cp_2Fe]^+PF_6^-$ is formed as a result of anion exchange. Thus the reaction of Cp_2Fe with HgX_2 (X = Cl or Br) ultimately involves the oxidation of ferrocene, in contrast to ruthenocene, which forms adducts with HgX_2.

When π-complexes with aromatic ligands are acted upon by HgX_2 salts, there is also a possibility of the mercuration of the π-ligand with formation of the C–HgX bond, which is characteristic of ferrocene[48] and $CpM(CO)_3$ (M = Mn or Re).[49,50]

(c) *Derivatives of Group III elements* EX_3 (*E = B, Al, Ga, In, or Tl; X = halogen or organic group*). Examples of the interaction of Lewis acids derived from Group III elements with transition metal complexes via both the metal and via the ligands (bridging and terminal CO groups, N_2, NO, CN and halogens) are known. The interaction with the oxygen atoms of the briding ligands is more characteristic of aluminium derivatives than of other Lewis acids. This leads to interesting features of the behaviour of transition metal complexes in reactions with aluminium compounds, which will be discussed below.

Numerous reactions of transition metal complexes, containing bridging carbonyl groups, with Lewis acids have been investigated: $[CpFe(CO)_2]_2$ with BX_3 (X = Cl or Br);[35] $[CpFe(CO)]_4$ with $AlBr_4$ and BX_3 (X = F, Cl, or Br);[35] $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$, and $Ru_3(CO)_{12}$ with $AlBr_3$;[35,60] $[CpNi(CO)]_2$ and $Cp_3Ni_3(CO)_2$ with AlR_3 (R = Et or iso-C_3H_7) and BF_3.[7,35] It has been shown by infrared spectroscopy and in a number of instances also by X-ray diffraction that the bond in the resulting donor–acceptor adducts is formed via the bridging CO groups. The American chemist Schriver, whose studies have been surveyed in a review[8], has made a considerable contribution to the study of the basicity of bridging carbonyl groups.

Table 5. The stretching vibration frequencies of the CO groups [ν(CO), cm^{-1}] in the adducts of $[CpFe(CO)_2]_2$ with Lewis acids[35]

Complex	Terminal CO groups	Bridging CO groups	
		free	coordinated
$[CpFe(CO)_2]_2$	1971; 1930	1797; 1765	—
$[CpFe(CO)_2]_2AlEt_3$	1993; 1985	1828	1682
$[CpFe(CO)_2]_2 \cdot BCl_3$	2038; 2020	1845	1463

It is noteworthy that, when Lewis acids are coordinated to bridging CO groups, the shifts of the ν(CO) stretching vibration frequencies are significantly different for adducts with different Lewis acids (Table 5).[35] Apparently the difference in the frequency shifts reflects qualitatively the strength of the donor–acceptor bond formed. The greater the degree of charge transfer and correspondingly the more stable the complex formed, the greater should be the changes in the vibration frequencies of the CO groups resulting from coordination to the Lewis acid.

However, estimation of the strength of the donor–acceptor interaction solely from the vibration frequency shifts is not always legitimate. The vibration frequencies can be influenced significantly also by other factors, which have no direct bearing on the change in the electronic structure of the donor molecules as a result of charge transfer on coordination. Thus an increase in vibration frequency can be caused also by kinematic factors. For carbonyl compounds, where coordination takes place via the oxygen atom of the CO group, estimation of the strength of the donor–acceptor bond from the ν(CO) frequency shifts can constitute a fair approximation, since the stretching vibrations of the carbonyl groups are highly localised and the changes in the vibration frequencies are predominantly caused by charge transfer from the oxygen atom to the acceptor molecule, i.e. by electronic effects.

Thus, according to infrared spectroscopic data, the compounds BX_3 are stronger acceptors than AlX_3. The replacement of the halogen in Al derivatives by electron-donating organic groups (Me, Et, Ph) weakens the acid properties. The observed regular variation of the ν(CO) and $\nu(N_2)$ frequency shifts in the spectra of the complexes *trans*-$ReClL_4X$ (X = CO or N_2) on coordination to aluminium derivatives as a function of R in AlR_3 is consistent with this observation[61]:

Complex	ν(CO), cm^{-1}	$\Delta\nu$(CO), cm^{-1}
trans-ReCl(CO)($Ph_2PCH_2CH_2PPh_2$)$_2$	1803	—
trans-ReCl($Ph_2PCH_2CH_2PPh_2$)$_2$(CO → $AlMe_3$)	1677	−126
trans-ReCl($Ph_2PCH_2CH_2PPh_2$)$_2$(CO → $AlPh_3$)	1653	−150
trans-ReCl($Ph_2PCH_2CH_2PPh_2$)$_2$(CO → $AlCl_3$)	1630	−173

Thus the shift increases with enhancement of the electron-accepting properties of the Lewis acid.

There are many examples in the literature indicating the possibility of the coordination of the terminal CO, N_2, and NO ligands in transition metal complexes to aluminium derivatives: *trans*-$ReClL_4X$ (X = CO or N_2) with AlR_3 (R = Me, Ph, or Cl);[61] ML_4X_2 (X = CO or N_2; M = Mo or W) with AlR_3 (R = Me, Et, or Ph) and $GaMe_3$;[61–63] $OsCl_2L_3(N_2)$ with $AlMe_3$ [61] (L = phosphine ligands; L_2 = chelating diphosphine ligands); (π-$Ph_3P^+-C_5H_4^-$)Mo(CO)$_3$ with $AlMe_3$;[37] $[CpW(CO)_3]^-Na^+$ with $AlPh_3$;[64] $W(CO)_5L$ (L = PPh_3, $P(OPh)_3$, or $P(n\text{-}C_4H_9)_3$] with $AlEtCl_2$ in the presence of O_2;[65] CpM(CO)(NO)L (M = Mo or W; L = CO or PPh_3) with $AlCl_3$;[22] $CpM(CO)_3$ (M = Mn or Re), π-AreneM(CO)$_3$ (M = Cr, Mo, or W), $CpV(CO)_4$, and some of their derivatives with $AlCl_3$.[25]

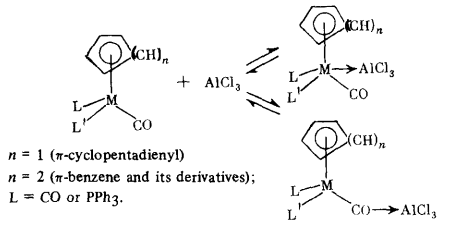
The study of the basicity of the atom Y or the coordinated ligand XY (CO or N_2) in the complexes *trans*-$ReCl(XY)L_4$ (L = PMe_2Ph) [61] relative to $AlMe_3$ solution in benzene showed that the N_2 ligand is more basic than the CO ligand in these compounds. Comparison of the equilibrium constants for the reactions

$$AlMe_3 \cdot Et_2O + ReCl(XY)L_4 \underset{80°}{\overset{C_6H_6}{\rightleftharpoons}} Et_2O + ReCl(XY \rightarrow AlMe_3)L_4$$

led to this conclusion.

The complexes $CpIr(CO)(PPh_3)$ with $TlCl_3$,[59] Cp_2MH_2 (M = Mo or W) with BX_3 (X = F or Cl) and AlR_3 (R = Me, Et, or Ph),[66,68] Cp_2ReH with BF_3 [66] and $AlMe_3$,[67] and Cp_2Ti with $AlEt_3$ [69] give rise to 1:1 adducts, in which the presence of M–M′ bonds is postulated.

Lokshin et al.[28] made the first systematic study of the interaction of a large number of carbonyl π-complexes of Group V–VII transition metals with $AlCl_3$. Investigation of a series of complexes of the same metal with different ligands or of isotypical complexes with different central metal atoms made it possible to determine the influence of the nature of the ligands and the central metal atom in the complex or the reactivity and the mode of reaction with $AlCl_3$. It has been shown that, depending on the nature of the complex itself and on the solvent, $AlCl_3$ can be coordinated either via the metal atom or via the CO group, or via both centres simultaneously:



n = 1 (π-cyclopentadienyl)
n = 2 (π-benzene and its derivatives);
L = CO or PPh_3.

This leads to completely different changes in the carbonyl region of the infrared spectrum, so that the formation of adducts of a particular type can be deduced spectroscopically. For example[28], the ν(CO) frequencies are 1931 and 2027 cm^{-1} for $CpRe(CO)_3$, 1740, 1991, and 2054 cm^{-1} for $CpRe(CO)_2$(CO → $AlCl_3$), and 2055, 2074, and 2130 cm^{-1} for $Cp(CO)_3Re \rightarrow AlCl_3$.

As mentioned above (Section IV), the mode of reaction depends on the solvent employed. Coordination via the metal atom and via the CO group was promoted by carrying out the reaction in CH_2Cl_2 and in benzene respectively. Thus the formation of adducts via the CO group in CH_2Cl_2 solution was observed only for $CpM(CO)_3$ (M = Mn or Re) and ring-substituted CTM derivatives: $(PhCH_2C_5H_4)Mn(CO)_3$ and $(Et_5C_5)Mn(CO)_3$. Apart from these complexes, in benzene solutions simultaneous interaction via both the oxygen atom of the CO ligand and the metal atom was observed also for $CpMn(CO)_2PPh_3$, $(Et_5C_5)Mn(CO)_2PPh_3$, $(C_6H_6)Cr(CO)_3$, $(1,3,5\text{-}Me_3C_6H_3)Cr(CO)_3$, $(Me_6C_6)Cr(CO)_3$, $(C_6H_6)W(CO)_3$, $CpV(CO)_4$, and $CpV(CO)_3PPh_3$.[28]

Competition between these two reactions is probably determined by the relative basicities of the metal and the oxygen in the complex and the relative strengths of the resulting bonds, the difference between the energies being evidently small. The weaker the basic properties of the metal atom in the complex the greater the predominance of the coordination via the CO group and, conversely, the more basic the metal atom, the more characteristic is the interaction via this centre. Complexes in which the metal atom is most basic do not give rise to adducts via the CO ligand in either CH_2Cl_2 or in benzene: CpMn(CO)(diphos), $CpRe(CO)_2PPh_3$, $CpNb(CO)_4$, $(C_6H_6)Cr(CO)_2PPh_3$, $Fe(CO)_4PPh_3$, and $Fe(CO)_3(PPh_3)_2$.[28]

The interaction of the cyanide complexes $K_4[Fe(CN)_6]$, $K_2[Ni(CN)_4]$, $Fe(phen)_2(CN)_2$ (phen = 1,10-phenanthroline), and $Fe(CNR)_4(CN)_2$ (R = H, Me, or Et) with boron halides has been investigated[70,71] and it has been shown that the adducts formed contain cyanide bridges between the transition metal and BX_3 (for example, $-\overset{|}{\underset{|}{Ni}}-C\equiv N-BF_3$), each CN group being linked to the Lewis acid.

A complex pattern in the carbonyl region of the spectrum (Table 6) is observed for the interaction of *trans*-$RhX(CO).(EPh_3)_2$ with BX_3 (X = halogen; E = P or As).[25,26] As mentioned above, different cases are possible, involving the formation of a donor–acceptor adduct or oxidative addition; nor can one rule out the possibility of interaction via the halogen ligand. In all these cases, the spectral changes in the region of the vibrations of the CO group are different. The most marked changes in ν(CO) apparently occur in oxidative addition and smaller changes correspond to the formation of a donor–acceptor adduct. The hypsochromic

shifts of the signal frequencies on coordination to a halogen are usually small (15–20 cm^{-1}).

It is believed that *trans*-$RhCl(CO)(PPh_3)_2$ forms a donor–acceptor adduct with BCl_3 via the rhodium atom[26]. However, $\nu(CO)$ for the adduct is displaced only by 23 cm^{-1} (Table 6); for such a small shift, coordination of the acid to a chlorine atom is more probable.

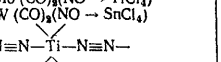
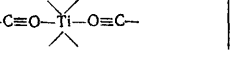
Table 6. Infrared spectra (in the region of the stretching vibrations of the CO group) of the adducts of the complexes *trans*-$[RhCl(CO)(EPh_3)_2]$ with BX_3.

Complex	Lewis acid	Compn. of adduct	ν(CO), cm^{-1}	$\Delta\nu$(CO), cm^{-1}
trans-$[RhCl(CO)(PPh_3)_2]$	—	—	1968	—
Ditto	BCl_3	1:1	1991	+23
Ditto	BBr_3	1:1	2098 w, 1990 s	+130, +22
trans-$[RhBr(CO)(PPh_3)_2]$	—	—	1969	—
Ditto	BBr_3	1:1	2102 w, 2049 m, 1998 w, 1985 s	+133, +80, +29, +16
trans-$[RhCl(CO)(AsPh_3)_2]$	—	—	1967	—
Ditto	BBr_3	1:1	2101 m, 2047 s	+130, +80

The infrared spectra of other adducts of rhodium complexes with BX_3 contain two or more bands in the region of the CO vibrations. There is apparently a possibility of the formation of different products simultaneously. Judging from the infrared spectra, the adduct *trans*-$RhBr(CO)(PPh_3)_2$ can contain molecules of the rhodium complex coordinated to the Lewis acid via the halogen ligand (1998, 1985 cm^{-1}), a donor–acceptor adduct (2049 cm^{-1}), and the oxidative addition product (2102 cm^{-1}).[25,26]

As mentioned above, the corresponding iridium complex *trans*-$IrCl(CO)(PPh_3)_2$ interacts with BF_3 via the metal atom, as shown by the hypsochromic shift of $\nu(CO)$ by 100 cm^{-1} (from 1967 to 2067 cm^{-1}).[16] The interaction of the same complex with $AlMe_3$ leads to an increase of the stretching vibration frequency of the CO group by 12 cm^{-1}. The formation of an adduct via the iridium atom has been postulated[61]. However, the above value of $\Delta\nu(CO)$ is more likely to indicate the coordination of $AlMe_3$ via the chlorine atom. The interaction of the same complex with $SnCl_4$ (see above, Section II). leads to $\Delta\nu(CO)$ or 113 cm^{-1} for the oxidative addition product and 74 cm^{-1} for the donor–acceptor adduct[17].

Table 7. Adducts formed via the ligands of transition metal complexes with Lewis acids of the type MX_4.

Complex	Lewis acid	Adduct	Refs.
$CpCr(NO)_2Cl$	$SnCl_4$	$CpCr(NO)_2(Cl \rightarrow SnCl_4)$	22
$CpMo(CO)_2(NO)$	$TiCl_4$	$CpMo(CO)_2(NO \rightarrow TiCl_4)$	22
$CpW(CO)_2(NO)$	$SnCl_4$	$CpW(CO)_2(NO \rightarrow SnCl_4)$	22
trans-$(Me_2PhP)_4ReCl(N_2)$	$TiCl_4$		79
trans-$(Me_2PhP)_4ReCl(CO)$	$TiCl_4$		79

Complexes containing halogen ligands as a rule react with Lewis acids via the halogen atom. Adducts of this type have been obtained for the following complexes: $Mn(CO)_5X$, $(PMe_3)_2Fe(CO)_2X_2$ (X = Cl, Br, or I), and $(PMe_3)_2Ni(CO)I_2$ with AlX_3 (X = Cl or I), $FeCl_3$, and $SbCl_5$;[72] $RuCl_2(CO)_2.(PMe_3)_2$ with $FeCl_3$;[73] $MoCl_2(NO)_2(PMe_3)_2$ with $FeCl_3$;[73] $CpRe(CO)_2Br_2$ with $AlCl_3$;[28] $CpCr(NO)_2Cl$ with $AlCl_3$, $SnCl_4$,[22] and FeCl;[73] $CpFe(CO)_2X$ (X = Cl, Br, or I) with a large set of Lewis acids[73].

According to the shifts of the $\nu(CO)$ frequencies for the adducts compared with the initial complex, in the case of $CpFe(CO)_2$ (X→M′X) the Lewis acids investigated can be arranged in the following sequence in terms of their electron-accepting properties: $SbCl_5 \cong AlCl_3 \cong FeCl_3 > MoCl_5 \cong GaCl_3 \cong AlBr_3 > FeBr_3 \cong AlI_3 > GaI_3 > NbCl_5 > SnCl_4 > InCl_3 \cong TiCl_4 > HgCl_2 \cong Cl_2 > I_2 > Br_2$.[73]

(d) The halides MX_4 of Group IV elements (M = Ti, Ge, or Sn). Numerous reactions of transition metal complexes with Lewis acids derived from Group IV elements and leading to the formation of oxidative elimination products have been described in the literature[12,13,74–78]. However, in the present review only those reactions are considered in which the initial complex enters wholly into the composition of the adduct. Data for the reversible formation of TMC adducts with Lewis acids $M'X_4$ are presented in Tables 7 and 8.

Table 8. Examples of the interaction of MX_4 with complexes via the transition metal atom.

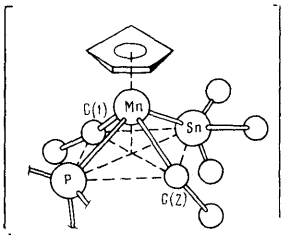
Complex	Lewis acid	Refs.
trans-$IrCl(CO)(PPh_3)_2$	$SnCl_4$	17
$CpM(CO)(NO)(PPh_3)$ (M = Mo, W)	$SnCl_4$	22
$(Et_2C_2)Mn(CO)_3$	$SnCl_4$	23
$CpMn(CO)_2L$ (L = PPh_3, $P(OPh)_3$ etc.)	$SnCl_4$	23, 80
$CpMn(CO)L_2$ (L_2 = diphosphine ligands)	$GeCl_4$, $SnCl_4$, $SnBr_4$, $TiCl_4$	23
$CpRe(CO)_3$	$TiCl_4$	22
$CpRe(CO)_2L$ [L = P(OPh)$_3$, P(OEt)$_3$, PPh_3]	$SnCl_4$, $SnBr_4$, $TiCl_4$	22
(1, 3, 5-$Me_3C_6H_3$) $M(CO)_3$(M = Cr, Mo, W)	$SnCl_4$, $TiCl_4$	22
$(C_6H_6)Cr(CO)_2PPh_3$	$SnCl_4$	22
Cp_2Ru	$SnCl_4$, $SnBr_4$	56
$(Ph_3P^+—C_5H_4^-)M(CO)_3$(M = Cr, Mo, W)	$TiCl_4$	22

In the majority of the cases investigated the interaction of the Lewis acids $M'X_4$ with complexes takes place via the transition metal atom and coordination via the ligand lone electron pair has been observed in only a few instances (Table 7). The adducts $[(PMe_2Ph)_4ReClL]_2.TiCl_4$ or more involved compounds containing solvent molecules, for example, $[ReCl(N_2)(PMe_2Ph)_4]_2.TiCl_4.THF$ (THF = tetrahydrofuran), and $[ReCl(N_2)(PMe_2Ph)_4]_2.TiCl_4.(C_6H_6)_n$ (n = 1–5), have been isolated[79] after the interaction of the compounds *trans*-$(PMe_2Ph)_4ReClL$ (L = CO or N_2) with $TiCl_4$. The decrease of the stretching vibration frequencies of the CO and N_2 groups indicates the coordination of $TiCl_4$ via these groups:

trans-$(PMe_2Ph)_4ReCl(N_2) + TiCl_4 \xrightleftharpoons{C_6H_6}$ *trans*-$[(PMe_2Ph)_4ClRe—N\equiv N—Ti—N\equiv N—ReCl(PMe_2Ph)_4].(C_6H_6)_{1-5}$. The $\nu(N_2)$ frequency of the initial complex (1925 cm^{-1}) shifts to 1814 cm^{-1} in the spectrum of the reaction product. This is the first example of a complex containing two nitrogen bridges.

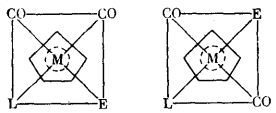
The cyclopentadienyl and arene derivatives of manganese, rhenium, chromium, molybdenum, and tungsten carbonyls [$CpM(CO)_3$, M = Mn or Re; $(Arene)M(CO)_3$, M = Cr, Mo, or W; and their various derivatives] in solutions combine reversibly with Lewis acids derived from Group IV elements

($SnCl_4$, $SnBr_4$, $TiCl_4$, $GeCl_4$) via the transition metal atom[22,23]. The characteristics of the influence of the nature of the metal (see Section II, 2) and the ligands (Section II, 3) on the basicity of the complexes have been examined in relation to these complexes. Solid adducts, having the 1:2 composition, of a series of complexes $CpMn(CO)_2L$ (where $L = PPh_3$, trialkylphosphines, $AsPh_3$, or $SbPh_3$) with $SnCl_4$ have been isolated[23]. X-Ray diffraction studies showed that, for $L = PPh_3$, the adduct has the ionic structure $[(C_5H_5)Mn(CO)_2(PPh_3)SnCl_3]^+SnCl_5^-$ and contains the Sn–Mn bond (with a length of 2.589 Å). The coordination environment of the manganese atom consists of a distorted square pyramid with the C_5H_5 ligand apical. Two CO groups (the OC–Mn–CO angle is 115°), the $SnCl_3$ group, and the PPh_3 ligand are located in the base of the pyramid *trans* to one another[80] (see Figure).



The structure of the cation $[C_5H_5Mn(CO)_2(PPh_3)(SnCl)]^+$.[80] Bond lengths (Å): Mn–P = 2.367, Mn–Sn = 2.589, Mn–C(1) = 1.82, Mn–C(2) = 1.83; valence angles: C(1)–Mn–P = 80.0°, C(2)–Mn–P = 79.6°, C(1)–Mn–C(2) = 115.1°, C(2)–Mn–Sn = 74.4°, C(1)–Mn–Sn = 74.9°, and P–Mn–Sn = 131.1°.

We may note that the addition of the acceptor E to the pseudotetrahedral complexes $(C_5H_5)M(CO)_2L$ can give rise to two isomers with the geometry of a square pyramid, which differ by the *cis*- or *trans*-disposition of the CO groups (or phosphorus nuclei, see below) in the base of the pyramid:



It has been shown by ^1H, ^{13}C, and ^{31}P NMR that, particularly in the protonation ($E = H^+$) of the complexes $CpM(CO)_2L$ and $CpM(CO)L_2$ ($M = Mn$ or Re; L and L_2 are mono- and bi-dentate phosphines), the products are both *cis*- and *trans*-isomers[81–83]. The infrared spectra of the adducts $[(C_5H_5)Mn(CO)_2(L).SnCl_3]^+SnCl_5^-$ in CH_2Cl_2 as a rule exhibit four and not two ν(CO) bands; the solutions apparently contain a mixture of isomers[23,80].

For $CpRe(CO)_2L$ [$L = PPh_3$, $P(OEt)_3$, or $P(OPh)_3$], the interaction with SnX_4 (X = Cl or Br) leads to the appearance of two new ν(CO) bands in the infrared spectra of the solutions in each case, i.e. only one isomer is formed in this instance. At the same time, a sharp change in the ratio of the ν(CO) band intensity ratios for the adducts is observed compared with initial compounds; this corresponds to an appreciable increase of the angle between the carbonyl groups (from ~100° to ~125°), which is possible only for the *trans*-isomer[22]. On the other hand, the reactions of these complexes with $TiCl_4$ apparently lead to the formation of a mixture of isomers [four ν(CO) infrared bands are observed][22].

There is a further series of examples of the reversible addition of Lewis acids $M'X_4$ to transition metal complexes (Table 8). In particular, the addition of $(Cpylid)M(CO)_3$ ($Cpylid = Ph_3P^+-C_5H_5^-$, M = Cr, Mo, or W) to $TiCl_4$,[22] of *trans*-$(PPh_3)_2Ir(CO)Cl$ to $SnCl_4$,[17] and of $CpM(CO)(NO).PPh_3$ (M = Mo or W) to $SnCl_4$ [22] involves interaction via the metal atom.

The reactions of ferrocene with SnX_4 and TiX_4 (X = Cl or Br) have been investigated. It is suggested that they involve the formation of salt-like products containing the ferrocenium cation and the $Sn_2X_9^-$ and $Ti_3X_{12}^-$ counterions[84]. In contrast to Cp_2M (M = Fe or Ni), ruthenocene is not oxidised under the influence of SnX_4 (X = Cl or Br) but gives rise to yellow products having the composition $2Cp_2Ru.3SnX_4$,[56] for which the structure $[Cp_2Ru–SnX_2–RuCp_2]^{2+}(SnX_5^-)_2$ has been proposed.

Table 9. The interaction of transition metal complexes with metal ions.

Transition metal complex	Reagent	Reaction product*	Refs.
$[Mn(CO)_4L]^-$ (L = CO, PMe_2, Ph, PPh_3, $P(OPh)_3$)	$M^+ = Li^+$, Na^+	$(CO)_3LMn-CO...M^+$	85,86
$[Fe(CO)_3(NO)]^-$	$M^+ = Na^+$, K^+, $(Ph_3P)_2N^+$	$(CO)_3Fe-NO...M^+$	87
$Fe(CO)_5$	$Cd(AsF_6)_2$	$Cd[(Fe(CO)_5)_2]^{2+}(AsF_6^-)_2$	88
$Fe(CO)_5$	$Sn(SbF_6)_2$	$Sn[(Fe(CO)_5)_2]^{2+}(SbFe_6^-)_2$	88
$Fe(CO)_5$	$Fe(SbF_6)_2$	$Fe[(Fe(CO)_5)_2]^{2+}(SbF_6^-)_2$	88
$[Mn(CO)_5)_2]_2$ $[CpMo(CO)_3]_2$ $[CpFe(CO)_2]_2$ $CpFe(CO)_2$ $[Co(CO)_3L]_2$ (L = $PMePh_2$, PPh_3, $P(C_4H_9)_3$	Mg amalgam in the presence of bases; B = THF, tetramethylethylenediamine, or pyridine	$M'C=O...(B_4Mg)...O=CM'$ or $M'C=O...(B_2Mg)...O=CM'$ or $M'-(B_2Mg)-M'$	89,90
$CPW(CO)_3^-$	Al, Al amalgam in THF	$[CpW(CO)_3]_3Al(THF)_3$	91

*The structures of the reaction products have been confirmed[89,91] by X-ray diffraction; $M' = Mn(CO)_4$ in the case of $[Mn(CO)_5]_2$.

2. Reactions with Metal Cations

Metal cations can play the role of electrophiles in relation to TMC (Table 9). The nature of the infrared spectra of the salt-like complexes $M^+[Mn(CO)_4L]^-$ [IV, M = Li or Na; L = CO, PMe_2Ph, PPh_3, or $P(OPh)_3$] [84,85] and $M^+[Fe(CO)_3(NO)]^-$ [V, M = Na, K, or $(Ph_3P)_2N$] in the carbonyl region in THF shows that they exist in two forms in equilibrium—contact ion pairs, where the alkali metal cation interacts with the oxygen atom of the CO ligands of complex (IV) or the NO ligand of complex (V), and ion pairs separated by the solvent. For complexes (IV), the existence of contact ion pairs in solution also follows from conductimetric and kinetic data for their reactions with alkyl halides[86]. When reagents binding alkali metal cations, namely crown-ethers or hexamethylphosphoramide, are added to solutions of the complexes in THF, the ν(CO) bands of the contact ion pairs (M–X≡O.....M', where X = C or N) disappear and only the bands of the free ions remain. Iron pentacarbonyl, which is a weak base, reacts in liquid SO_2

with strong acids—$Cd(AsF_6)_2$, $Sn(SbF_6)_2$, and $Fe(SbF_6)_2$.[88] On the basis of Mössbauer and infrared spectroscopic data, the following structure of the reaction product has been postulated: $[-Fe-M-Fe-]^{2+}.2(EF_6)^-$, where E = As or Sb; thus Lewis acids interact with $Fe(CO)_5$ via the metal atom.

Under the influence of magnesium amalgam, the dimeric complexes $[Mn(CO)_5]_2$, $[CpMo(CO)_2L]_2$, $[CpFe(CO)_2]_2$, and $[Co(CO)_3L]_2$ (L is a phosphine ligand) undergo reductive cleavage in the presence of bases such as pyridine, THF, and tetramethylethylenediamine with formation of the compounds $B_xMg(m)_2$ (B = base, m = group containing a transition metal, and $x = 2$ or 4 depending on the nucleophilic properties of the metal carbonyl group)[89,90]. In tetracoordinate complexes ($x = 2$) the transition metal can be linked to the Mg^{2+} ion both via CO bridging groups (Mg–O≡C–M) and directly (M–Mg). The interaction of groups containing a transition metal with Mg^{2+} in hexacoordinate complexes ($x = 4$) always proceeds via the oxygen atoms of the CO groups[90].

According to X-ray diffraction data[89], the adduct $[CpMo(CO)_3]_2Mg(Py)_4$ has an octahedral structure, the Mg atom being coordinated to four pyridine molecules in the equatorial plane and to the oxygen atoms of two metal carbonyl groups—one from each $CpMo(CO)_3$ residue.

3. Reactions with Halogens, Antimony Pentachloride, and Alkyl Halides

When TMC react with halogens, the X_2 molecules are polarised and the positively charged cation X^+ always adds to the transition metal atom, the coordination number of the central atom increases by unity, and ionic compounds $[L_nMX]^+$ are formed via the mechanism:

$$L_nM + \overset{\delta+}{X}-\overset{\delta-}{X} \rightarrow [L_nMX]^+X^- \text{ or } [L_nMX]^+X_3^- .$$

In a number of cases nucleophilic attack by the X^- anion in the second stage of the reaction leads to the formation from these ionic compounds of oxidative addition or oxidative elimination products, for example[92,93]:

$$Mo(CO)_3(diphos)_2 + I_2 \rightarrow [Mo(CO)_3(diphos)_2I]^+I^- \rightarrow Mo(CO)_2(diphos)_2I_2$$
$$CpRe(CO)_3 + Br_2 \rightarrowtail [CpRe(CO)_3Br]^+Br^- \rightarrow CpRe(CO)_2Br_2 + CO .$$

The reactions with the halogens are known for the octahedral derivatives of chromium, molybdenum, and tungsten hexacarbonyls of the type $M(CO)_{6-n}L_n$ (where L are electron-donating ligands: amines, phosphines, and arsines; $n = 2-4$): $M(CO)_2(L_2)_2$ (L_2 = bidentate phosphine or arsine)[92,94,95]; $(CO)_3M(L_2)_3M(CO)_3$ (L_2 = bridging bidentate phosphine)[95]; $Mo(CO)_4L_2$;[96] $Mo(CO)_3(Amine)_3$ and $Mo(CO)_3Q$ (Q = tridentate amine)[97]; $M(CO)_3Q'$ [M = Mo or W; Q' = polydentate phosphine ligands $PhP(C_6H_4PPh_2\text{-}o)_2$ or $P(C_6H_4.PPh_2\text{-}o)_3$].[98] The addition of halogens has been described for the following π-complexes: (π-Arene)$M(CO)_3$ (M = Mo or W; Arene = $Me_nH_{6-n}C_6$);[99]# $CpMn(CO)_3$;[100] $CpIr(CO)(PPh_3)$;[59] Cp_2Ru.[101]#

When TMC are acted upon by $SbCl_5$, Cl_2 is apparently formed initially as a result of the reaction $SbCl_5 \rightarrow SbCl_3 + Cl_2$ and then Cl^+ adds to the metal atom in the complex and Cl^- adds to a second $SbCl_5$ molecule. For example, the interaction of $CpRe(CO)_3$ with $SbCl_5$ leads to the formation of $[CpRe(CO)_3Cl]^+SbCl_6^-$.[102] The interaction of (π-Arene).$M(CO)_3$ (M = Mo or W),[103] Cp_2Ru,[56] and $[Re(CO)_3]_2$(porphyrin)[104]# with $SbCl_5$ leads to analogous products.

#The structure of the reaction products has been confirmed by X-ray diffraction analysis.

The reaction of $Mo(CO)_3L_3$ with $SbCl_5$ and $FeCl_3$ results in the formation of $[Mo_2(CO)_4L_4(\mu\text{-}Cl)_3]^+X^-$ ($X^- = SbCl^-$ or $FeCl_4^-$).[105]

The positive species adds to the central metal atom when TMC are acted upon by alkyl halides or stronger alkylating agents—trialkyloxonium salts and dialkyl sulphates. These reactions proceed via the mechanism $L_nM + \overset{\delta+}{R}-\overset{\delta-}{X} \rightarrow [L_nM-R]^+X^-$. Depending on the nature of the central atom M, the ligand environment, and X^-, the second reaction stage may involve the migration of R to CO with simultaneous attack by X^-, for example:

$$\underset{L=PPh_3}{CpM(CO)L} + MeI \rightarrow [CpM(CO)(L)Me]^+I^- \rightarrow \underset{M=Co,\ Rh}{CpM(COMe)(L)I} \quad (3)$$
$$M=Ir$$

In relation to this reaction, it is possible to follow the influence of various structural factors[24]. The dicarbonyl complexes $CpM(CO)_2$ do not interact with MeI, since the basicity of the central atom is in this case insufficient. The rate of the bimolecular reaction (3) increases in the sequence Co < Rh ≪ Ir, the rate constants 10^4k amounting to 25.7, 35.0, and 210 litre mol^{-1} s^{-1} respectively. For M = Co and Rh, the reaction does not stop at the first stage and neutral acyl complexes are formed immediately. However, in the case of M = Ir, where the basicity of the central atom is extremely high, the final product is an ionic complex. The rate of reaction depends greatly on R and L: for CpCo(CO)L and MeI, the relative rate increases with enhancement of the electron-donating properties of L in the sequence PPh_3 (25.7) < PPh_2Me (150) < $PPhMe_2$ (330). The dependence of the rate on the solvent in the sequence THF < acetone < CH_2Cl_2 < MeCN shows that there is appreciable charge separation in the transition state.

It is possible to quote a further series of examples of similar reactions of transition metal complexes with alkylating agents: of $W(CO)_2(diphos)_2$ with $[Et_3O]^+BF_4^-$;[106] of $CpM(CO)(PPh_3)$ (M = Co, Rh, or Ir) with MeI and EtI;[24] of $CpIr(CO)(PPh_3)$ with MeCl, MeBr, $C_6H_{13}I$, $C_6H_5CH_2I$, and C_3H_7I;[59] of $CpCoL_2$[107] and FeL_5[108] [L = $P(OMe)_3$] with MeI.

4. Oxidation under the Influence of Electrophiles

When the transition metal atom in the complex is sufficiently basic (in the presence of strong electron-donating ligands), the influence of certain electrophiles can lead to oxidation with electron transfer to the acceptor and the formation of a donor radical-cation: $(L_nM)^0 \overset{-e}{\rightarrow} (L_nM)^+$. There is then a possibility of two cases: (a) the neutral acceptor A accepts an electron and gives rise to the radical-anion A^-, i.e. the reaction product is the radical-ion pair $(L_nM^+)(A^-)$; (b) the cationic acceptor A^+ accepts an electron and is converted into a neutral molecule A ("one-electron oxidation"). The formation of radical-ion pairs is characteristic of the most basic complexes in reactions with π-acids (tetracyanoethylene and others). These reactions will be considered in detail below.

In one-electron oxidation reactions the oxidants are usually $NO^+PF_6^-$, diazonium salts, and the silver salts $AgPF_6$ and $AgBF_4$. They accept an electron from the TMC with formation of compounds or species which leave the reaction sphere, displacing thereby the equilibrium in the direction of the formation of the products [$NO^+ \rightarrow NO$; $Ag^+ \rightarrow Ag$ (metallic); diazonium salts → $Ph^{\cdot} + N_2$]. 18-Electron transition metal complexes are converted into 17-electron paramagnetic radical-cations, which give rise to well resolved EPR spectra and possess a magnetic moment corresponding to a single

unpaired electron. We may note that electrochemical as well as chemical oxidation is possible. Measurement of the half-wave potential $E_{1/2}$ permits hypotheses concerning the possibility of the chemical oxidation of the same substrates.

The conversion of the diamagnetic 18-electron complexes into radical-cations is always accompanied by an increase of the ν(CO) infrared frequencies, on average by 100–140 cm^{-1}. There are data[109] showing that the ferrocenium ion can also serve as a one-electron oxidant. It is then converted into ferrocene. We may note in this connection that, among the reactions of metallocenes with various electron acceptors, ferrocene and nickelocene are distinguished by their ability to give up readily one electron with formation of salts of the cations Cp_2Fe^+ and Cp_2Ni^+.

The reactions of Cp_2Fe with metal halides such as MX_4 (M = Ti or Sn; X = Cl or Br), $VOCl_3$, and $SbCl_5$ lead to the formation of the solid salts $Cp_2Fe.3TiX_4$, $Cp_2Fe.2SnX_4$, $Cp_2Fe.VOCl_3$, and $2Cp_2Fe.SbCl_5$, which always contain the Cp_2Fe^+ cation.[84] The compound Cp_2Ni is oxidised under the influence of $TiCl_4$ to $Cp_2Ni^+TiCl_4$.[84] On reaction with the sandwich-type acceptor Cb_2Ni, where $Cb = (3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-}$,[84] ferrocene gives rise to a charge-transfer complex (CTC), which is gradually converted into the salt $Cp_2Fe^+.Cb_2Ni^-$. The reaction of Cp_2Ni with Cb_2Ni leads to complete electron transfer and the formation of an ionic compound in which both the cation and anion are sandwich complexes with a central Ni^{3+} ion.

Chemical oxidation reactions have been studied for the following complexes: $(C_6Me_{6-n})Cr(CO)_2(PhC{\equiv}CPh)$ (n = 0, 1);[110] CpFe(diphos)R (R = Me, H, Cl, Br, I, or $SnMe_3$);[111] $CpFe(CO)_nL_{2-n}X$ [n = 0, 1, L = $P(OPh)_3$ or CNPh];[111] $CpMn(CO)L_2$ [L_2 = diphos or $(PPh_3)_2$];[111] $CpV(CO)_2$(diphos) and $CpV(CO)_3L$ (L = PPh_2Me);[112] $Fe(CO)_2L$(diene) [L = CO, PPh_3, or $P(OCH_2)_3CH$)];[113] $Fe(CO)_3L_2$ (L = PPh_3, PPh_2Me, $P(OPh)_3$, or $P(NMe_2)_3$, L_2 = diphos);[114] $CpMn(CO)_2L$ (L = phosphines);[115] $[HCoL_4]^+PF_6^-$;[109] $Cr(CO)_4$(diphos) and $[Cr(NO)(MeCN)_3(diphos)]^+$.[116]

5. Reactions with π-Acids

When transition metal π-complexes react with π-acids, there is a possibility of the formation of charge-transfer complexes with complete electron transfer from the donor to the π-acid in the ground electronic state and the formation of salts of radical-anions.

$$D + A \rightleftarrows D \cdot A\ (CTC) \rightleftarrows D^+ + A^- \rightarrow \text{secondary products}$$

(radical-anion salt)

For weakly bound CTC, the transfer of electron density from the donor to the acceptor in the ground electronic state is slight, while the excited states are structures with complete electron transfer from D to A (i.e. are ionic). When a light quantum $h\nu_{CT}$ is absorbed, the CTC passes from the ground to an excited state and a charge transfer band (CTB) appears in the electronic spectrum. The formation of CTC leads to hardly any changes in the infrared spectra of the donor and acceptor, which is due to the fact that the shift of electron density fron the donor to the acceptor in the ground state is slight. Thus an appreciable displacement of the absorption bands of $(Arene)Cr(CO)_3$ and 1,3,5-trinitrobenzene (TNB) was not observed in the infrared spectra of their CTC.[117] When the electron transfer in the ground electronic state is complete, significant changes in the vibrational and electronic spectra are observed; one may then expect the appearance of an EPR signal.

The spectral changes when the transition metal π-complexes interact with π-acids can be illustrated in relation to the reactions of the manganese complexes $CpMn(CO)_3$, (Et_5C_5).$Mn(CO)_2(PPh_3)$, and CpMn(CO)(diphos) with tetracyanoethylene (TCE) and tetracyanoquinodimethane (TCQD).[118] The interaction of $CpMn(CO)_3$ and $(Et_5C_5)Mn(CO)_2(PPh_3)$ with TCE in CH_2Cl_2 does not lead to changes in the infrared spectra either in the carbonyl region [although the ν(CO) frequencies are extremely sensitive to changes in the distribution of electron density in the molecule] or in the region corresponding to the ν(CN) vibrations of TCE; nor do signals appear in the EPR spectra. New CTB bands, which are absent from the spectra of the initial compounds, appear in the electronic spectra (at 790 and 740 nm respectively).

When a solution of TCQD was added to one of CpMn(CO).(diphos) in CH_2Cl_2, a sharp colour change from yellow to emerald green and the appearance of an EPR signal were observed. At −150 °C the EPR spectrum of the complex CpMn(CO)(diphos).TCQD (VI) in CH_2Cl_2 showed two signals superimposed on one another: one broad signal, apparently due to $[CpMn(CO)(diphos)]^+$, and another, narrow signal due to the presence of TCQD. The electronic spectra of a solution of (VI) also indicate the presence of the TCQD radical-anion. The infrared spectrum of (VI) differs significantly from the spectra of the initial components: the frequencies ν(CO) are displaced by ~100 cm^{-1} towards higher values (as in oxidation by the Ag^+ ion and other oxidants), while the ν(CN) bands of TCQD are displaced towards lower values by ~50 cm^{-1}. These data lead to the conclusion that CpMn(CO)(diphos) undergoes one electron oxidation under the influence of TCQD.

The kinds of products formed in the reactions of transition metal π-complexes with π-acids (CTC or radical-anion salts) depend on the polarity of the solvent and on the relative strength of the donor and the π-acids involved in the interaction. Polar solvents should promote electron transfer and the formation of CTC is more likely in a medium with a low dielectric constant. For example, the CTC $Cp_2Fe.TCE$, which exists in the solid state and in solution in cyclohexane, dissociates in acetonitrile[119,120]:

$$Cp_2Fe \cdot TCE \rightleftarrows Cp_2Fe^+ + TCE^-$$

The complexes $(Arene)Cr(CO)_3$ form CTC with TNB, *p*-benzoquinone, TCE, and chloranil (CA),[117,121–123] the most stable CTC being formed with TNB.[117,121] The stronger π-acids may promote a more complete electron transfer. In solution the starting materials and the reaction products are involved in an equilibrium whose position depends on the concentration; in dilute solutions the equilibrium is displaced towards the starting materials.

In benzene solutions EPR signals due to mixtures of $(Arene)Cr(CO)_3$ with π-acids (TNB, CA, and TCE) have not been observed, while in nitromethane the signals due to radicals have been noted[121]. Thus the chromium complex is oxidised in a polar solvent.

Solid adducts with π-acids have been obtained for a number of π-complexes. Thus $(C_6H_6)_2Cr$, which is very readily oxidised to $(C_6H_6)_2Cr^+$, like ferrocene, gives rise to solid 1:1 salts with TCE, TNB, CA, and *p*-quinone, which are stable in air[124]. The oxidation of $(C_6H_6)_2Cr$ by π-acids has been demonstrated convincingly by various methods—EPR, infrared spectroscopy, and electronic spectroscopy. The EPR spectrum of each adduct contains two signals corresponding to $(C_6H_6)_2Cr^+$ and the radical-anions of the π-acids.

Solid adducts of Cp_2Co and Cp_2Ni with CA^- and TNB have been isolated: $Cp_2Co.CA$, $Cp_2Co.2CA$, $Cp_2Ni.2CA$, and $Cp_2Co.TNB$. The 1:1 adducts are CTC, in contrast to the

1:2 adducts, which are salt-like[125]. The above adducts of the complexes Cp_2M are relatively stable in air compared with the initial Cp_2Co or Cp_2Ni, which are unstable as regards oxidation. Ferrocene also forms complexes in solution with *p*-benzoquinone[125], CA,[125] TCQD,[126] TCE,[119,120,123] tetrachlorophthalic anhydride[125], and TNB.[127] The complexes Cp_2M (M = Ru or Os) are oxidised by TCE in acetonitrile with formation of salts of Cp_2M^+.[123]

The solid complex CpMn(CO)(diphos).TCQD, which, as in solutions, has the structure of the salt $[CpMn(CO)(diphos)]^+$. $.TCQD^-$ (EPR and infrared spectra), has been isolated from benzene solution[118].

The problem of the relative orientations of the donor and acceptor molecules in the CTC has been discussed in some studies. According to X-ray diffraction data[122], the TNB molecules in the adduct $(MeC_6H_5)Cr(CO)_3$.TNB are located in planes which are approximately parallel to the planes of the arene rings and the planes passing through the oxygen atoms of the CO groups in the chromium complex. The distance between the planes of the cyclic ligand and the TNB molecule is 3.41 Å, while the plane of the oxygen atoms of the CO groups is separated from the plane of the other acceptor molecule by 2.97 Å. Thus both the arene ring and the CO groups should be involved in the formation of the complex. (2,5-Dimethyldecamethylene-*ansa*-benzene)tricarbonylchromium also forms a complex with TNB.[123] It is postulated in this case that the acceptor molecules form a bond with the CO groups of the chromium complex, since the π-ring is blocked by the bridge with ten CH_2 units. However, this evidence is not convincing, because the decamethylene ring, being fairly long, can bend away and need not block the benzene ring.

The nature of the influence of substituents in the arene ring of the complexes $Arene(CO)_3$ on the frequencies of the charge-transfer bands in the spectra of CTC with TCE has been investigated[128]. The satisfactory correlation between the position of the CTB and the σ^+ constant of the substituent in the aromatic ring led the authors to postulate that, in the formation of the CTC, TCE interacts with the aromatic ring of the arenechromiumtricarbonyl derivatives,

VI. CONCLUSION

It has been shown from extensive experimental data that the TMC possess distinct basic properties and readily interact with a wide range of aprotic acids. The interaction can be both via the central metal atom and via the ligands.

One of the main centres where the acid–base interaction takes place is the transition metal atom. The manifestation of basic properties has been noted for virtually all Group V–VIII transition metals. There are not data for the basic properties of Group III and IV metal (Sc, Y, lanthanides, and titanium and its analogues) complexes as well as complexes in which the metal has the d^{10} configuration and which contain Cu^+, Ag^+, Zn^{2+}, Cd^{2+}, and Hg^{2+}. Thus basic properties are most characteristic of the complexes of metals with partially filled *d*-orbitals containing not less than four *d* electrons.

Allowance for the possibility of the interaction via the metal atom permits a new approach to the problem of the study of the mechanisms of the reactions of TMC, particularly the reactivity of π-complexes containing cyclic π-ligands. Evidently, one cannot regard the reactions of these compounds with electrophiles simply by analogy with the reactions of the free ligands without taking into account the role of the central atom and its ligand environment. Such reactions include the so-called aromatic substitution reactions [characteristic of ferrocene, $(C_5H_5)Mn(CO)_3$ derivatives, and certain other π-complexes]: isotope exchange between hydrogen and acids, acylation, alkylation, mercuration, etc. Throughout the initial period of these studies, it was traditional to compare the rates of these reactions and the properties of the π-complexes and the corresponding benzene derivatives. However, such comparison is apparently not legitimate. Although many reactions of π-complexes and aromatic compounds proceed under similar conditions, their mechanisms can be significantly different.

It was demonstrated above with numerous examples that aprotic acids (aluminium, tin, and iron halides) form adducts with many π-complexes via the central atom or via the ligands. The same halides catalyse Friedel–Crafts alkylation and acylation—reactions characteristic of many π-complexes (ferrocene, cymantrene, etc.). In considering the mechanisms of such reactions, it would therefore be incorrect to ignore the possibility of adduct formation; despite the similarity of conditions, the mechanism of the acylation of organometallic π-complexes can differ significantly from the mechanism of the acylation of benzene and its analogues. It would be no exaggeration to state that, as data on the basicity of TMC accumulate, demonstration is obtained the "ricochet" substitution mechanism, proposed more than 20 years ago by Nesmeyanov and coworkers[129,130], according to which the attack by the reagent is directed initially to the central metal atom, after which there is a change of direction from the metal to the cyclic π-ligand. Many examples of reversible rearrangements of this type with migration of a proton[131–133] as well as alkyl and other groups[134,135] have been found recently. The ricochet substitution mechanism has been used to account for the mechanism of the acid exchange of hydrogen in cyclic π-ligands (cyclopentadienyl, benzene) in iron, manganese, chromium, and rhenium complexes[136]. The ideas concerning the basicity of the complexes and the important role of the central metal atom can be used to explain the specificity, kinetics, and nature of the products of many other reactions of π-complexes with electrophiles, for example, the cleavage of the M–C σ-bonds and metal–metal bonds under the influence of hydrogen halides, halogens, and mercury salts HgX_2.

In conclusion, at present the extensive data concerning the basicity of the TMC contain virtually no quantitative data based on the study of the kinetics and thermodynamics of the interaction of the TMC with various electrophiles and that the entire data available are so far purely qualitative.

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