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BASICITY OF TRANSITION METAL CARBONYL COMPLEXES

IX *. AN INFRARED STUDY OF LEWIS ACID REACTIONS WITH CYCLOPENTADIENYL AND ARENE DERIVATIVES OF GROUPS VI AND VII TRANSITION METAL CARBONYLS AND NITROSYLS

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Summary

The different courses of the interactions of cyclopentadienyl and arene derivatives of Group VI and VII transition metal carbonyl and nitrosyl complexes with Lewis acids, in solutions, have been studied by IR spectroscopy.

The formation of adducts involving the metal atom was observed for $CpRe(CO)_2L$ (L = CO, PR_3) with $SnCl_4$, $SnBr_4$, $TiCl_4$; $AreneM(CO)_3$ (M = Cr, Mo, W) with $SnCl_4$, $TiCl_4$; and $Ph_3PC_5H_4M(CO)_3$ (M = Cr, Mo, W) with $TiCl_4$ and $AlCl_3$. Complexes $CpM(CO)_2NO$ and $CpM(CO)(NO)PPh_3$, depending on their donor and acceptor nature, form adducts involving the oxygen atoms of CO or NO groups or the metal atom. $CpCr(NO)_2Cl$ reacts with Lewis acids via the chlorine atom. The relative basicity of the different sites in the complexes investigated is discussed.

Introduction

Earlier [1] the phosphine derivatives of cyclopentadienylmanganesetricarbonyl (CMT) have been found to react reversibly with Lewis acids, in solution, giving adducts. Reactions of Lewis acids with CMT derivatives via the manganese atom are accompanied by high-frequency shift (by 100—150 cm^{-1}) of the CO stretching vibrations in the IR spectra, which is similar to the shifts observed in the course of protonation of these complexes [2]. The CMT itself does not react with $SnCl_4$, however, when the CO group is replaced by a donor phosphine ligand the metal basicity increases and adduct formation is made possible. The metal basicity is still higher when one more phosphine ligand is added to CMT, the weaker Lewis acids, $SbCl_3$, $GeCl_4$ and $HgCl_2$ may produce adducts [1].

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* For part VIII see ref. 3.

With $AlCl_3$ the reaction may yield two adducts: at the metal and at the oxygen atom of the carbonyl group [3]. The reaction path depends on the nature of the complex and the solvent employed. Adduct formation at the oxygen results in the essential decrease of the CO stretching frequency of the coordinated CO group, simultaneously the frequencies of free CO groups increase by 20—50 cm^{-1}.

The present work is concerned with the IR study of reactions of different Lewis acids with the derivatives of cyclopentadienylrheniumtricarbonyl (CRT); arenetricarbonyls of chromium, molybdenum and tungsten; cyclopentadienylide complexes of chromium, molybdenum, tungsten and manganese; cyclopentadienylcarbonylnitrosyl complexes $CpM(CO)_2NO$, $CpM(CO)(NO)PPh_3$ (M = Mo, W) and $CpCr(NO)_2Cl$.

Results and discussion

1. Cyclopentadienyl and arene carbonyl complexes of rhenium, chromium, molybdenum and tungsten

The CO stretching frequencies of the complexes investigated, in methylene chloride solution, are listed in Table 1. CRT and CMT, studied previously [1], do not react with $SnCl_4$ in methylene chloride. CMT also does not react with the stronger acid $TiCl_4$. However, with CRT, in the presence of excess $TiCl_4$, together with the bands due to the initial compound there appeared new bands, shifted to higher frequencies by more than 100 cm^{-1}, the latter being specific for metal adducts.

This agrees with our previous results on the protonation of CMT and CRT phosphine derivatives, that in these complexes the rhenium basicity is higher than that of manganese [4]. Substitution of a CO group by phosphine, or phosphite ligands sharply increases the metal basicity [2,4,5]. Thus, $CpRe(CO)_2L$ compounds where L = PPh_3, $P(OEt)_3$ or $P(OPh)_3$ react not only with $TiCl_4$ but with $SnCl_4$ and $SnBr_4$ as well. The initial complexes are transformed completely into adducts in the presence of excess $SnCl_4$. Even with a large excess of $SnBr_4$ incomplete transformation of the less basic $CpRe(CO)_2P(OPh)_3$ complex into adduct was observed. Thus the Lewis acids form the following series of decreasing basicity in their ability to form adducts: $TiCl_4 > SnCl_4 > SnBr_4$.

Recently it was found that formation of *cis* and *trans* isomers, with respect to phosphine ligand, is possible in protonation of CMT phosphine derivatives [6,7]. Similar possibilities exist in reactions with Lewis acids.

Evidence as to the geometry of Lewis acid addition may be obtained from analysis of the intensity ratios of the symmetric and antisymmetric CO stretching modes in the starting complex and adduct. Approximate IR intensities of the CO stretching bands are determined by the change of CO bond dipole moments in the process of vibration.

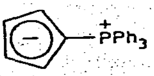
Thus, one may show [8] that the relative intensity of the CO stretching bands is determined by the angles between CO bonds; for the $M(CO)_2$ fragment: $A_{as}(CO)/A_s(CO) = \mathrm{ctg}\,\alpha/2$, where α is the angle between CO bond directions and A_s and A_{as} are the integrated intensities of bands of symmetric and antisymmetric CO vibrations. When the angle is almost 90° this ratio is close to unity, which actually takes place in the case of free donor molecules. Thus, for $CpRe(CO)_2P$-

TABLE 1

THE CO STRETCHING FREQUENCIES FOR COMPLEXES INVESTIGATED AND THEIR ADDUCT WITH LEWIS ACIDS

Formula	ν CO (cm^{-1}) in CH_2Cl_2 solution	
	Donor	Adduct
$CpRe(CO)_3$	1929s 2027s	
$CpRe(CO)_3 + SnCl_4$	1929s 2027s	
$CpRe(CO)_3 + TiCl_4$	1928vs 2027s	2082m 2138m
$CpRe(CO)_2P(OPh)_3$	1891s 1961s	
$CpRe(CO)_2P(OPh)_3 + SnCl_4$	1891s 1961s	2010s 2060m
$CpRe(CO)_2P(OPh)_3 + SnBr_4$	1891m 1961m	2002s 2053m
$CpRe(CO)_2P(OPh)_3 + TiCl_4$	1891m 1961m	2021s 2073s
$CpRe(CO)_2P(OEt)_3$	1871s 1945s	
$CpRe(CO)_2P(OEt)_3 + SnCl_4$	1871m 1943m	2003s 2055m
$CpRe(CO)_2P(OEt)_3 + TiCl_4$	—	2000s 2023(sh) 2061s 2083(sh)
$CpRe(CO)_2PPh_3$	1859s 1930s	
$CpRe(CO)_2PPh_3 + TiCl_4$	—	1990s 2017m 2051m 2074m
$MzCr(CO)_3$ ^{a}	1882s 1961s	
$MzCr(CO)_3 + SnCl_4$	1881s 1961s	2005s 2030m 2065s
$MzCr(CO)_3 + TiCl_4$	1882s 1961s	1997s (br) 2069s
$C_6H_6Cr(CO)_2PPh_3$	1834s 1893s	
$C_6H_6Cr(CO)_2PPh_3 + SnCl_4$	—	1958s 2002 s-m
$MzMo(CO)_3$	1881s 1963s	
$MzMo(CO)_3 + SnCl_4$	—	2012s 2038m 2081s
$MzMo(CO)_3 + TiCl_4$	—	(dec.)
$MzW(CO)_3$	1876s 1961s	
$MzW(CO)_3 + SnCl_4$	—	2001s 2023m 2075s
$MzW(CO)_3 + TiCl_4$	—	1995s 2030m 2070s 2091s
$CpylidCr(CO)_3$ ^{b}	1813s 1918s	
$CpylidCr(CO)_3 + CF_3COOH$ in CH_2Cl_2	—	1956s 1971(sh) 2036s
$CpylidCr(CO)_3 + TiCl_4$	—	1950s 1963(sh) 2032s
$CpylidCr(CO)_3 + AlCl_3$	—	1950s 1964(sh) 2032s
$CpylidMo(CO)_3$	1811s 1911s	
$CpylidMo(CO)_3 + CF_3COOH$ in CH_2Cl_2	—	1958s 1970(sh) 2045s
$CpylidMo(CO)_3 + TiCl_4$	—	1962s (br) 2044s
$CpylidMo(CO)_3 + AlCl_3$	—	1961s (br) 2043s
$CpylidW(CO)_3$	1808s 1904s	
$CpylidW(CO)_3 + CF_3COOH$	—	1954s (br) 2040s
$CpylidW(CO)_3 + TiCl_4$	—	1957s (br) 2040s
$CpylidW(CO)_3 + AlCl_3$	—	1953s (br) 2040s

^{a} Mz = mesitylene. ^{b} Cpylid =



$(OEt)_3$ the ratio of optical densities of the bands is 1.28. It is important to remember that the use of optical densities, instead of the integrated intensities, is valid only at the same band halfwidths, which is approximately true in the given case. Such an approximation is sufficient for the rough estimation of the change in angle upon coordination with an acceptor. The intensity ratio varies considerably upon $SnCl_4$ coordination with this molecule: $D_{as}(CO)/D_s(CO) = 3.37$ which indicates a considerable increase of the angle between CO groups in the adduct (approximately from 104° to 147°).

Analogous behaviour is observed in coordination with $SnBr_4$. Assuming that the carbonyl groups, phosphine ligand and the coordinated acceptor molecule are located in the base of a tetragonal pyramid with the transition metal atom at the vertex, such an increase in the angle is only possible with *trans*-located acceptor and phosphine ligand. Upon coordination with H^+ and $AlCl_3$ the angle increase is negligible and no unequivocal conclusion may be drawn on the adduct geometry, although formation of the *trans* isomer seems more probable.

In reaction of $CpRe(CO)_2PR_3$ with $TiCl_4$ unlike other Lewis acids, the IR spectrum pattern of the adduct in the region of $\nu(CO)$ is more complicated, 3—4 bands are observed instead of 2 $\nu(CO)$ bands. The additional bands are less intensive and shifted by 20—30 cm^{-1} towards the higher frequences, with respect to the principal adduct bands. The intensity ratios of the principal and additional bands changes with time which enables us to ascribe them to different substances in solution. On the addition of water all four bands disappear and the bands of the initial carbonyl complex are observed. A similar pattern has been obtained earlier, in reaction of some phosphine CMT derivatives with Lewis acids [1]. Additional bands may be due either to formation of adducts of different composition or to a simultaneous presence of *cis* and *trans* adducts.

In reaction with $SnCl_4$ coordination at the metal also takes place for the arene derivatives of Group VI metals, $MzM(CO)_3$ (Mz = mesitylene. M = Cr, Mo, W), which is obvious from the data of Table 1. With excess $SnCl_4$ the Mo and W complexes are converted entirely into the adduct, while the Cr adduct is at equilibrium with the starting compound. This result displays an increase of metal basicity in the complex with increasing atomic number. This agrees with our results on protonation [9] and with the regularities observed for other Group V—VII metal complexes [2,4]. Introduction of phosphine ligand increases the transition metal basicity, thus $C_6H_6Cr(CO)_2PPh_3$ converts almost completely into the adduct in the presence of an excess of $SnCl_4$.

Arene complexes of Group VI metals with $TiCl_4$ also produce adducts bound at the metal atom. The molybdenum complex decomposes simultaneously, however, whereas the tungsten derivative shows four (instead of two) bands due to the adduct. The two bands are close to those of the $TiCl_4$—$MzCr(CO)_3$ adduct and the two additional bands are shifted to the higher frequencies by 20—35 cm^{-1}. The band pairs belong to different substances since their relative intensities change with time. All changes in the spectra are reversible and when the adducts are decomposed with water the bands of the initial compounds appear again. Thus additional bands may be explained by formation of different adducts in solution. We note that for some tricarbonyl complexes the adduct formation reduces the local symmetry of the $M(CO)_3$ fragment, as has been mentioned for $AlCl_3$ adducts [3]. As a result, instead of two CO stretching modes of A_1 and E species (local C_{3v} symmetry), observed in the spectra of initial complexes, the adducts show three bands due to the splitting of the degenerate modes into two components.

2. *Cyclopentadienylide complexes* $(C_5H_4PPh_3)M(CO)_3$ *(M = Cr, Mo, W)*

It has been demonstrated by IR and NMR methods [10] that cyclopentadienylide complexes $(C_5H_4PPh_3)M(CO)_3$ (where M = Cr, Mo and W) are protonated in CF_3COOH and react with BF_3 at the metal atom. Our results on protonation (Table 1) agree with this conclusion and show that the metal is exclusively basic in these complexes. CpylidCr(CO)$_3$ is almost completely protonated in a 1/100 mixture of CF_3COOH/CH_2Cl_2, while for $C_6H_6Cr(CO)_2PPh_3$ the protonation is incomplete in a 1/10 mixture. Thus, replacement of benzene by Gpylid increases the basicity of the central metal atom much more than carbonyl replacement by triphenylphosphine. The Lewis acids, $TiCl_4$ and $AlCl_3$, also react with ylide complexes in CH_2Cl_2 solution with adduct formation at the metal atom. Recently we have found [3] that $AlCl_3$ may react with transition metal carbonyls in two ways: at the metal and at the carbonyl oxygen, depending essentially on the nature of the solvent. In benzene adduct formation at the CO ligand is more favourable than in CH_2Cl_2 solution. CpylidMo(CO)$_5$ gives a solid, oxygen coordinated adduct with $AlMe_3$ [11] which is isolated from toluene solution. Ylide complexes are poorly soluble but dissolve upon addition of $AlMe_3$. The complexes studied are insoluble in benzene even in the presence of $AlCl_3$. In CH_2Cl_2 the coordination with $AlCl_3$ occurs via the metal, the high basicity of which favours such a reaction course.

Unlike the neutral ylide complexes of Cr, Mo, and W the cationic ylide complex [CpylidMn(CO)$_3$]$^+PF_6^-$ reacts with none of the Lewis acids investigated ($SnCl_4$, $TiCl_4$, $AlCl_3$) and is not protonated in CF_3COOH. The presence of the positive charge thereby decreases considerably both the metal and carbonyl oxygen basicity.

3. *Carbonylnitrosyl complexes CpM(CO)$_2$NO and CpM(CO)(NO)PPh$_3$ (M = Mo, W)*

Table 2 presents the data on reaction of the carbonylnitrosyl complexes CpM(CO)$_2$NO (M = Mo, W) and their phosphine derivatives with Lewis acids. With respect to the compounds described before in this paper these complexes have an additional basic centre - the nitrosyl oxygen atom.

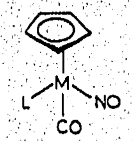
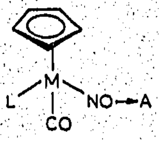
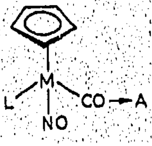
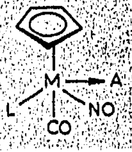
The interaction of the compounds with complexes of the type Cp$_3$Ln (where Ln is a lanthanide) has been reported [12]. This occurs via the nitrosyl oxygen which is more basic than that of the carbonyl. We found that, depending on the structure of carbonylnitrosyl complexes and the acceptor, interaction may occur at the nitrosyl group, central metal atom or the carbonyl oxygen.

The present and earlier data [1] show that $SnCl_4$ and $TiCl_4$ yield the adducts with carbonyl complexes at the transition metal atom. The adduct CpMo(CO)$_2$-NO=TiCl$_4$ is formed via the nitrosyl oxygen but CpW(CO)$_2$NO decomposes in reaction with $TiCl_4$. $SnCl_4$ does not react with CpMo(CO)$_2$NO but gives the nitrosyl oxygen adduct with the tungsten analogue. This result confirms the higher basicity of nitrosyl oxygen in the tungsten complex than that in the molybdenum compound. This may be a consequence of the stronger electron density shift from tungsten towards the nitrosyl ligand compared with molybdenum towards nitrosyl, owing to the d_π—p_π interaction.

The phosphine complexes CpM(CO)(NO)PPh$_3$, with higher metal basicity, react with $SnCl_4$ to give the metal adducts. In this case the stretching mode frequencies of CO and NO shift by 150 cm^{-1} towards the higher values. An increase in metal basicity upon addition of phosphine ligand makes this process more favourable than coordination via nitrosyl group. The complex decomposed in reaction with $TiCl_4$.

TABLE 2

THE CO AND NO STRETCHING FREQUENCIES FOR CARBONYL NITROSYL COMPLEXES AND THEIR ADDUCTS

Formula	Frequencies (cm^{-1}) in CH_2Cl_2 solution							
								
	ν(NO)	ν(CO)	ν(NO)	ν(CO)	ν(NO)	ν(CO)	ν(NO)	ν(CO)
$CpMo(CO)_2NO$	1670s	1942s 2021s						
$CpMo(CO)_2NO + SnCl_4$	1670s	1945s 2020s						
$CpMo(CO)_2NO + TiCl_4$	1666s	1941s 2020s	1486m	2003(sh) 2065m				
$CpMo(CO)_2NO + AlCl_3$	1670s	1950s 2025vs	1450s	2025vs 2087vs	1710m	1735(sh) 2065m		
$CpW(CO)_2NO$	1660s	1929s 2011s						
$CpW(CO)_2NO + SnCl_4$	1658s	1929s 2011vs	1481m	1981m 2051m				
$CpW(CO)_2NO + AlCl_3$	1655s	1930s 2010vs	1450s	2010vs 2075s				
$CpMo(CO)(NO)PPh_3$	1606s	1914s						
$CpMo(CO)(NO)PPh_3 + SnCl_4$							1747s	2070s
$CpMo(CO)(NO)PPh_3 + AlCl_3$			1390s	1991s			1722m	2070m
$CpW(CO)(NO)PPh_3$	1595s	1900s						
$CpW(CO)(NO)PPh_3 + SnCl_4$							1740s	2050s
$CpW(CO)(NO)PPh_3 + AlCl_3$	1590m	1900m	1400s	1975s			1713m	2070m

Earlier for cyclopentadienyl and arene complexes of the Group V—VII metal carbonyls we have shown [3] that $AlCl_3$ may give the adducts either at the central metal atom or at the carbonyl oxygen. The reaction path depends on the

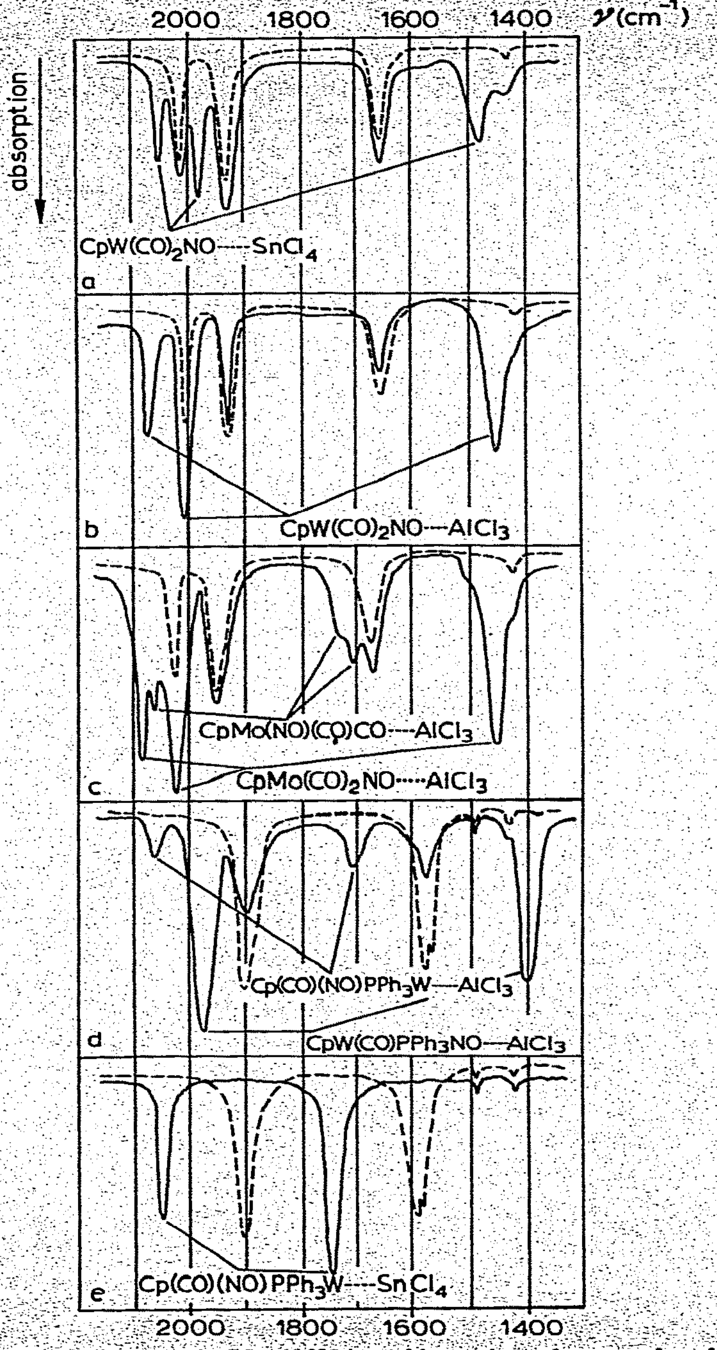


Fig. 1. IR spectra in CO and NO stretching regions of some carbonyl nitrosyl complexes in the presence of Lewis acids: a. $CpW(CO)_2NO + SnCl_4$, b. $CpW(CO)_2NO + AlCl_3$, c. $CpMo(CO)_2NO + AlCl_3$, d. $CpW(CO)(NO)PPh_3 + AlCl_3$, e. $CpW(CO)(NO)PPh_3 + SnCl_4$.

relative basicity of the metal and oxygen in the complex and also on the solvent employed. No reaction at the metal was observed for $CpM(CO)_2NO$ and $AlCl_3$. $CpW(CO)_2NO$ and $AlCl_3$ produce the nitrosyl oxygen adduct in CH_2Cl_2. The nitrosyl stretching frequency decreases from 1655 to 1450 cm^{-1} while the stretching frequencies of CO increase from 1929 and 2011 cm^{-1} to 2010 and 2075 cm^{-1}. One of the shifted frequencies overlaps with the band of the initial compound. The bands were assigned by making a comparison of their relative intensities.

The molybdenum compound $CpMo(CO)_2NO$ displays specific behaviour towards $AlCl_3$. The lower nitrosyl oxygen basicity with respect to the tungsten analogue (see above) results in the fact that there is competitive coordination at the carbonyl and nitrosyl oxygens, although interaction via nitrosyl oxygen prevails. When the carbonyl adduct formation occurs one of the $\nu(CO)$ frequencies decreases to 1735 cm^{-1}, the $\nu(NO)$ frequency increases to 1710 cm^{-1} and the second $\nu(CO)$ band increases to 2065 cm^{-1}. In the case of the nitrosyl adduct the $\nu(NO)$ frequency decreases and $\nu(CO)$ increases to 1450, 2025 and 2087 cm^{-1} respectively.

In triphenylphosphine derivatives $CpM(CO)(NO)PPh_3$ the metal basicity is higher, resulting in competition between the metal and nitrosyl oxygen atoms in reaction with $AlCl_3$. The tungsten derivative shows bands at 1400 cm^{-1} ($\nu(NO)$), 1975 cm^{-1} ($\nu(CO)$) due to the oxygen adduct, bands at 1713 cm^{-1} ($\nu(NO)$), 2070 cm^{-1} ($\nu(CO)$) due to the metal adduct together with weak bands of the initial complex ($\nu(NO)$ 1590 cm^{-1}, $\nu(CO)$ 1900 cm^{-1}). If only coordination with the metal was observed for $SnCl_4$ then reaction at the oxygen prevails for $AlCl_3$, which is evident from the ratio of band intensities (Fig. 1). The molybdenum complex behaves analogously but the metal adduct content is higher than that of the tungsten complex which could be explained by somewhat lower nitrosyl oxygen basicity. No significant difference in behaviour was observed with $AlCl_3$ in CH_2Cl_2 and benzene.

Thus, depending on the relative basicity of the metal, carbonyl and nitrosyl oxygens and on the nature of the acceptor in the carbonylnitrosyl complexes, the different types of donor—acceptor interactions may take place with the metal or oxygens of the carbonyl and nitrosyl ligands acting as basicity centres.

$CpCr(NO)_2Cl$ gives with Cp_3Ln, in solutions of benzene and CH_2Cl_2, the nitrosyl oxygen adducts [12]. For reactions with $SnCl_4$ and $AlCl_3$ in CH_2Cl_2 we observed the high-frequency shifts of the $\nu(NO)$ bands from 1716 and 1820 cm^{-1} to 1735 and 1835 cm^{-1} (with $SnCl_4$) and 1743 and 1845 cm^{-1} (with $AlCl_3$). The 15—30 cm^{-1} shift is evidence of acceptor coordination with the halogen atom bound to the transition metal [13]. Such behaviour is specific for the complexes with a halogen ligand which was noted previously, for example with $CpRe(CO)_2Br_2$ in reaction with $AlCl_3$ [3].

Experimental

The IR spectra were recorded on UR-20 Zeiss IR spectrometer in the 1400—2200 cm^{-1} region. The benzene and CH_2Cl_2 solutions were prepared immediately prior to measurements. The Lewis acid excess was added under dry argon to solutions of the initial complexes.

All the compounds investigated were prepared by methods previously described.

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