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BASICITY OF TRANSITION METAL CARBONYL COMPLEXES

VIII*. AN INFRARED STUDY OF THE REACTION OF ALUMINIUM CHLORIDE WITH SOME CYCLOPENTADIENYL AND ARENECARBONYL TRANSITION METAL COMPLEXES

B.V. LOKSHIN*, E.B. RUSACH, Z.P. VALUEVA, A.G. GINZBURG and N.E. KOLOBOVA
Institute of Organo-Element Compounds, Academy of Sciences, Vavilova 28, Moscow B-312 (U.S.S.R.)

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Summary

The interaction of cyclopentadienyl and arene derivatives of carbonyl complexes of Group V, VI and VII transition metals with $AlCl_3$ in benzene and CH_2Cl_2 solutions has been studied by IR spectroscopy.

The formation of adducts involving the metal atom or the carbonyl oxygen atom was observed. The reaction path depends on the structure of the complex and on the nature of the solvent. In benzene the adduct formation at the CO ligand is more favourable than in CH_2Cl_2 solution. Introduction of a phosphine ligand in the place of the CO group or introduction of donor substituents into the π-ring increases the basicity of the central metal atom and makes adduct formation at the metal more probable.

The basicity of the metal atom in complexes with the same ligands increases with increase of atomic number in the group. $CpRe(CO)_2Br_2$ forms adducts with $AlCl_3$ at the bromine atoms (1/1 and 1/2). For $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$ complex formation takes place at the iron atom.

It is now commonly accepted that the cyclopentadienyl and arenecarbonyl transition metal complexes display the properties of bases. This has been confirmed by IR and NMR study of protonation [1-6] and reactions with Lewis acids such as $SnCl_4$, $GeCl_4$, $SbCl_3$ and $HgCl_2$ [7]. The formation of adducts with the Lewis acids as well as metal protonation result in a shift to higher frequency of CO stretching modes of more than 100 cm^{-1}.

Other possible donor centres in these molecules are the carbonyl oxygen and the π-ligand. Some examples are known that demonstrate their reactions

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* For part VII see ref. 6.

with strong π-acids at the π-ligands, affording charge transfer complexes [8]. Such interaction leads to certain changes in the electronic absorption spectra but practically leaves the CO stretching frequencies unaffected. The reactions occurring at the CO oxygen are known only for Lewis acids containing the Group III elements boron, gallium or aluminium.

The carbonyl complexes with bridged CO groups react with aluminium halides, AlX_3, and alkyl derivatives, AlR_3, via the oxygen atom of the bridged carbonyl [9-17]. Some reactions have been described for the aluminium derivatives with terminal CO groups: for $CpW(CO)_3^-$ anions, the molybdenum cyclopentadienylide complex $(Ph_3PC_5H_4)Mo(CO)_3$, and some complexes of the type $Mo(Phen)(PPh_3)(CO)_2$ and *trans*-$ReCl(CO)(PR_3)_4$ [18-26]. In some cases the structures of the adducts have been confirmed by X-ray analysis [27]. Such interaction results in a marked decrease in the frequency of the carbonyl group bonded with the Lewis acid, and a simultaneous increase in the frequencies of the non-bonded CO groups of 20-50 cm^{-1}.

If the carbonyl complex contains σ-bonded ligands with lone electron pairs, e.g. halogen or CN, then a Lewis acid may interact with such group [28,29]. Then the CO stretching frequencies increase by 30-50 cm^{-1}. It is also known that the interaction depends on the nature of Lewis acid. Thus the $CpW(CO)_3^-$ anion reacts with $AlPh_3$ via the carbonyl oxygen while in the case of $InPh_3$ the metal atom is involved [19]. Cyclopentadienylide molybdenum tricarbonyl reacts with a proton and BF_3 at the metal atom, and with $AlMe_3$ at the CO group [10,30]. We do not know the reactions of metal carbonyl complexes with Al derivatives at the metal atom, although the $AlMe_3$—metal adducts have been reported for $TiCp_2$ and Cp_2MH_2 (M = Mo, W) [31-33].

The present work is concerned with the IR study of reactions of the series of cyclopentadienyl and arene Group V, VI and VII metal carbonyls with $AlCl_3$ in solutions.

It was found that depending on the nature of complex and conditions of the reaction, the formation of adducts may occur at the metal atom as well as at the carbonyl oxygen.

Experimental

The IR spectra in the region of 1600-2200 cm^{-1} were recorded on a Zeiss UR-20 IR spectrometer. The solutions in dry, freshly distilled benzene and methylene chloride were prepared directly before measuring. The excess $AlCl_3$ was added to the solution of the initial complex in benzene or CH_2Cl_2 under argon.

Results and discussion

Recently it has been shown that the substitution of carbonyl ligand in cyclopentadienylmanganese tricarbonyl (CMT) with triphenylphosphine occurs in the presence of $AlCl_3$ in benzene solution at room temperature, whereas usually this reaction requires UV irradiation or heating at high temperature [34]. $AlCl_3$ is insoluble in benzene but the addition of CMT causes it to dissolve with a change of colour from yellow to cherry-red. The IR spectra in the $\nu(CO)$ region

TABLE 1

THE CO STRETCHING FREQUENCIES FOR INVESTIGATED COMPLEXES IN BENZENE AND CH_2Cl_2 SOLUTIONS

Formula	Solvent[a]	$\nu(CO)(cm^{-1})$ in solution	$\nu(CO)(cm^{-1})$ in solution in presence of excess $AlCl_3$	$\Delta\nu(CO)(cm^{-1})$		
				coord. CO group	free CO group	coord. at metal
$CpMn(CO)_3$	A	1938 2025	1747s[b] 1938vs 2001s[b] 2025vs 2056s[b] 2117w[c]	220	62	
	B	1938 2025	1743s 1938vs 2005s 2025vs 2059s 2080(sh) 2118w			126
$PhCH_2C_5H_4Mn(CO)_3$	A	1935 2021	1745s 1935m 2000s 2021m 2053s 2110w	219	63	
	B	1935 2022	1741m 1936s 2003m 2021s 2057m-s 2110w			110
$Et_5C_5Mn(CO)_3$	A	1920 2007	1725s 1920m 1985s 2007m 2039vs 2094m	224	63	
	B	1916 2005	1725m 1916s 1985(sh) 2005s 2035s 2051m 2094s			111
$CpMn(CO)_2PPh_3$	A	1875 1940	1688vs 1983vs 2000(sh) 2044s	220	76	
	B	1867 1934	1971m 2000w 2006s 2048s			127
$EtH_4C_5Mn(CO)_2PPh_3$	A	1871 1934	1683vs 1980s 2000(sh) 2038s	220	77	
	B	1864 1930	1966m 1991w 2000s 2041s			124
$Et_5C_5Mn(CO)_2PPh_3$	A	1857 1920	1685vs 1955s 1981s 2025s	203	73	
	B	1850 1915	1987s 2029s			128
$CpMn(CO)PPh_2\cdot(CH_2)_2PPh_2$	A	1838	1967s			
	B	1837	1965s			128
$CpRe(CO)_3$	A	1931 2027	1740s 1931w 1991s 2027w 2054s 2126m	223	60	
	B	1929 2027	1740m 1996m 2055vs 2074vs 2130s			124
$CpRe(CO)_2PPh_3$	A	1870 1935	1974s 2049s			
$CpRe(CO)_2Br_2$	A	2005 2068	2006s 2022s 2031(sh) 2070s 2083s 2096s			
	B	2006 2073	2006s 2040w 2073s 2097(sh)			
$C_6H_6Cr(CO)_3$	A	1900 1978	1668s 1976(sh) 2006(sh) 2015vs 2072s	258		
	B	1895 1974	2009s 2028(sh) 2078s			117
$C_6H_6Cr(CO)_2PPh_3$	A	1846 1900	1943s 1993s			
	B	1835 1893	1950s 2001s			113
$1,3,5\text{-}Me_3C_6H_3Cr(CO)_3$	A	1888 1972	1660vs 1953s 1991(sh) 2006vs 2061s	256	64	
	B	1882 1962	1997s 2015(sh) 2066s			117
$Me_6C_6Cr(CO)_3$	A	1875 1960[d]	1650s 1940s 1980(sh) 1995vs 2049s	254	64	
	B	1865 1950	1987s 2000(sh) 2055s			121
$1,3,5\text{-}Me_3C_6H_3Mo(CO)_3$	A	1886 1960[d]	1886s 1965s 2000s 2015m 2070s			
	B	1881 1963	2002s 2020(sh) 2075s			124
$C_6H_6W(CO)_3$	A	1896 1978	1661s 1896m 1951s 1996(sh) 2010vs 2074s	262	58	
	B	1897 1979	2007s 2024(sh) 2081s			113

continued

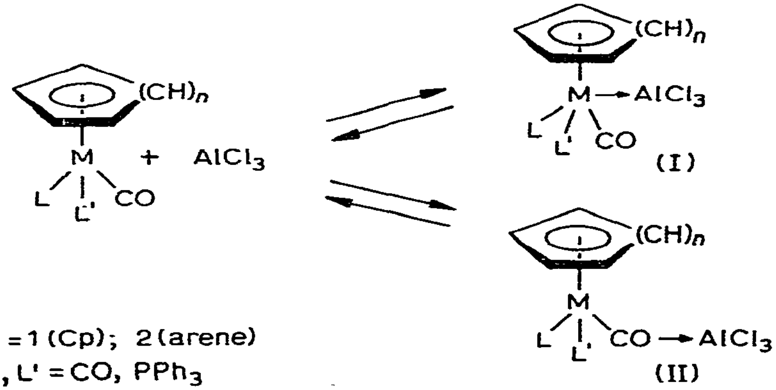
TABLE 1 (continued)

Formula	Solvent[a]	ν(CO)(cm^{-1}) in solution	ν(CO)(cm^{-1}) in solution in presence of excess $AlCl_3$	$\Delta\nu$(CO)(cm^{-1})		
				coord. CO group	free CO group	coord. at metal
$CpV(CO)_4$	A	1921 2035	1676s 1923vs 2000s 2029vs 2066s 2127m	272		
	B	1921 2030	2066s 2121s			127
$CpV(CO)_3PPh_3$	A	1859 1960[a]	1626s 1859s 1960s[d] 2007s 2033m 2078m	266		
	B	1855 1956	2022(sh) 2037s 2080s			157
$CpNb(CO)_4$	A	1921 2035	decomposition			
	B	1922 2036	2020m 2086s 2103(sh) 2141s			144
$Fe(CO)_4PPh_3$	A	1943 1970 2051	1943s 1970(sh) 2051m 2077s 2100(sh) 2148m			
	B	1941 1976 2051	2080s 2091(sh) 2099(sh) 2147s			115
$Fe(CO)_3(PPh_3)_2$	A	1890	2024s 2033(sh)			
	B	1886	2029s 2041(sh)			149

[a] A, benzene solution, B, CH_2Cl_2 solution. [b] Adduct at carbonyl oxygen atom. [c] Adduct at metal atom. [d] Benzene absorption.

of CMT in benzene with or without $AlCl_3$ are shown in Table 1 and Fig. 1. CMT in benzene shows two CO stretching modes at 1938 and 2025 cm^{-1} assigned respectively to the degenerate and symmetrical CO modes in the $Mn(CO)_3$ fragment with C_{3v} local symmetry. Upon addition of $AlCl_3$ a very strong band appears at 1747 cm^{-1} corresponding to the CO group bound with $AlCl_3$ at the oxygen atom (shifted over 220 cm^{-1} with respect to the mean CO frequency in CMT). On the other hand the spectrum contains two bands at 2001 and 2056 cm^{-1} shifted to higher frequencies (mean shift 62 cm^{-1}) corresponding to two free CO groups. Thus the IR spectral data confirm the generation of the $CpMn(CO)_2CO \rightarrow AlCl_3$ complex (II, Scheme 1). The formation of the bond with Lewis acid facilitates substitution of a CO group with triphenylphosphine. It is interesting to note that the character of the interaction with $AlCl_3$ depends on

SCHEME 1. TWO PATHS OF $AlCl_3$ ADDUCT FORMATION



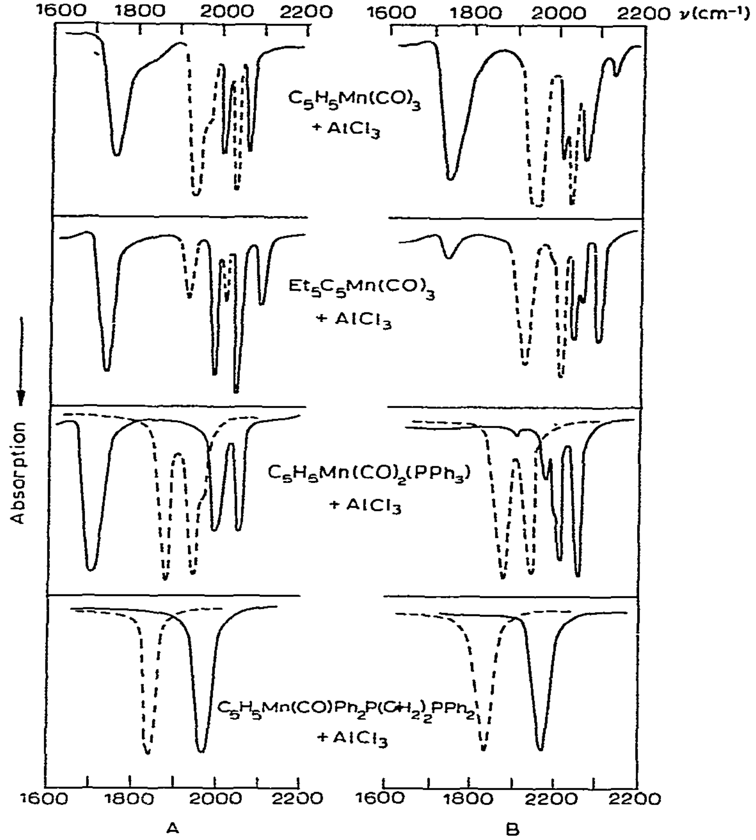


Fig. 1. IR spectra in CO stretching region of CMT derivatives in benzene (A) and CH_2Cl_2 (B) solutions in the presence of excess of $AlCl_3$.

the nature of the solvent. When aluminium chloride was added to the solution of CMT in CH_2Cl_2 the spectrum showed, along with the bands of free CMT and the $AlCl_3$ adduct at the oxygen atom, also bands at 2080 and 2118 cm^{-1} (average shift 126 cm^{-1} to higher frequencies) which could be assigned to the $AlCl_3$ manganese atom adduct (I, Scheme 1). The oxygen adduct band intensities decrease gradually while the metal adduct bands retain intensity, upon the solution standing. This interaction with a metal atom has not been observed earlier either for aluminium halides or their alkyl derivatives. CMT does not react with the weaker Lewis acids, e.g. $SnCl_4$. However, introduction of the stronger donor, ligand phosphine, instead of the carbonyl group, or introduction of donor substituents into the Cp ring, enhance the central metal atom basicity and makes it capable of metal adduct formation [7].

Thus we studied the reaction of $AlCl_3$ with CMT phosphine derivatives and with CMT derivatives containing donor substituents in the Cp ring (Table 1 and Fig. 1).

Introduction of donor substituents into the Cp ring of CMT does not materially affect the character of the interaction with $AlCl_3$. However, in CH_2Cl_2, the content of the form with the coordinated metal atom is higher, evident from the growth of relative intensities of the respective bands. Substitution of the carbonyl group by phosphine sharply increases the manganese atom basicity and facilitates interaction at the metal. No carbonyl group adducts were observed from the IR spectra of these compounds in CH_2Cl_2. Benzene solutions exhibit bands specific of both types of adducts, with approximately equal intensities at first. After some time (about 1.5 h for $CpMn(CO)_2PPh_3$) the bands specific of the CO group adduct disappear while the bands of the metal adduct remain. The formation of an oily precipitate is observed. Probably the metal adduct is more stable, while the CO adduct is less stable and transforms rapidly into other products in the course of further reactions. The formation of a carbonyl oxygen adduct along with the more stable metal—metal adduct may be explained kinetically. Introduction of the second phosphorus atom into the CMT molecule enhances further the metal atom basicity and provides no formation of carbonyl adducts, either in benzene or CH_2Cl_2.

Dependences similar to those of CMT derivatives are observed with other complexes studied in this work.

The higher the metal basicity in the complex (according to the protonation data [1-4]) the easier the coordination at the metal atom, and still less expressed will be the interaction of $AlCl_3$ with the oxygen atom. Interaction with oxygen in CH_2Cl_2 (besides manganese tricarbonyl complexes) was revealed only for cyclopentadienylrhenium tricarbonyl (CRT). In this case the spectrum shows bands of both types of adducts (I and II, Scheme 2). The absence of bands of free CRT and the high intensities of metal adduct bands agree with the higher basicity of rhenium than manganese in CRT. In benzene solution the majority of the complexes investigated interact with $AlCl_3$ via both metal atom and CO groups. The lower the metal basicity the greater the interaction at the CO group. It should be noted that the data of Table 1 are for freshly prepared solutions. The bands of carbonyl-coordinated adduct decrease or disappear upon the solution standing. In some cases the content of metal adduct may increase or remain practically constant. Probably two simultaneous processes occur in solution: decomposition of the adduct at the oxygen and its transformation into the metal adduct. The last process may proceed via complex dissociation into the starting products, which sometimes appear in the IR at higher intensities.

The formation of adducts due to coordination of $AlCl_3$ at the oxygen atom along with an interaction at the metal atom has been observed also for the complexes arene $M(CO)_3$ ($M = Cr, W$), $CpV(CO)_4$ and $CpV(CO)_3PPh_3$.

In $CpNb(CO)_4$ the metal basicity is rather high [4] and interaction at the metal atom only is observed in CH_2Cl_2, but in benzene the compound decomposes rapidly in the presence of $AlCl_3$, resulting in CO free products. The shift of the $AlCl_3$ coordinated CO mode depends weakly upon the metal basicity. It scarcely changes on introduction of a phosphinic ligand or with the change of metal atomic number in the group. On going from Group VII to VI to V derivatives the shift increases gradually.

Under similar conditions interaction at the metal atom only is observed in pentacarbonyliron derivatives $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$.

It is interesting to note that the local symmetry of the $M(CO)_n$ fragment does not remain usually for adducts with Lewis acids at the metal. In particular, in compounds with an $M(CO)_3$ group usually the doublet or the band with a shoulder are observed instead of *E* type degenerate modes of C_{3v} local symmetry. The symmetry distortion is explained by interaction with an acceptor molecule.

The action of $AlCl_3$ on $CpRe(CO)_2Br_2$ caused no shift of the CO stretching modes specific of the metal or CO group adducts. However, a high frequency shift (of nearly 20 cm^{-1}) observed is in good agreement with the shifts of CO bands upon $AlCl_3$ coordination with the halogen joined to the transition metal [29]. The presence of four bands shifted from the bands of the initial complex may serve as evidence of two different adducts.

$CpMn(CO)_2PPh_3$ and $EtC_5H_4Mn(CO)_2PPh_3$ give in CH_2Cl_2 solution in the presence of $AlCl_3$ two additional weak bands in the high frequency region together with strong bands of the adduct at the central atom. This resembles the appearance of extra bands when interaction occurs between phosphine CMT derivatives and $SnCl_4$ [7].

These additional bands in the spectra are either due to *cis—trans* isomerism of adducts or due to the formation of different types of complexes (e.g. 1/1 and 1/2).

These bands disappear if water is added to the solution as do the bands of the adducts linked to the metal atom. The bands of the initial compounds reappear.

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