Vibrational spectra and structure of "staircase" carbonyl π-complexes of transition metals

1. Electronic effects

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FTIR spectra have been studied for "staircase" cyclopentadienyl complexes comprising two or three metal carbonyl fragments bound by the metal-carbon bond $Cp(CO)_2Fe{-}CpmMn(CO)_3$ (**1**), $Cp(CO)_2Fe{-}CpmFe(CO)_2CH_2Ph$ (**2**), $Cp(CO)_2Fe{-}Cpm(CO)_2Fe{-}CpmMn(CO)_3$ (**3**), $Cp(CO)_2Mo{-}Cpm(CO)_2Fe{-}CpmMn(CO)_3$ (**4**), $Cp(CO)_3W{-}Cpm(CO)_2Fe{-}CpmMn(CO)_3$ (**5**), $Cp(CO)_2Fe{-}Cpm(CO)_2Fe{-}BmCr(CO)_3$ (**6**), $Cr(CO)_3Bm{-}CpmFe(CO)_2CH_2Ph$ (**7**), where Cp = η^5-C_5H_5, Cpm = η^1: η^5-C_5H_4, Bm = η^1:η^6-C_6H_5, as well as mononuclear model complexes $Cp(CO)_2Fe(CH)_2Ph$ (**8**), $CpMn(CO)_3$ (**9**), and (η^6-C_6H_6)$Cr(CO)_3$ (**10**). The spectra were interpreted on the basis of the local symmetry of each metal carbonyl center. The positions of νCOs are determined by the mutual electronic effect of each center. $CpmM(CO)_n$ groups are strong electron acceptors and cause an increase in νCOs of adjacent $M(CO)_n$ groups. $Cp(CO)_nM$ groups, being electron donors, cause a decrease in the frequencies of neighboring groups. In trinuclear complexes, the frequencies of the central $Fe(CO)_2$ group are not changed much due to the compensation of donor and acceptor influences of two neighboring substituents.

Key words: infrared spectra, π-complexes, metal carbonyls, electronic effects of substituents.

Recently, a number of homo- and heteronuclear π-complexes of the "staircase" type have been synthesized[1,2]. The complexes contain bridging organic ligands bound to the metal atom by either σ- or π-bonds. In this paper, IR spectra in the region of CO stretching vibrations (νCO) have been studied for di- and tri-nuclear complexes

$Cp(CO)_2Fe{-}CpmMn(CO)_3$ (**1**),
$Cp(CO)_2Fe{-}CpmFe(CO)_2CH_2Ph$ (**2**),
$Cp(CO)_2Fe{-}Cpm(CO)_2Fe{-}CpmMn(CO)_3$ (**3**),
$Cp(CO)_2Mo{-}Cpm(CO)_2Fe{-}CpmMn(CO)_3$ (**4**),
$Cp(CO)_3W{-}Cpm(CO)_2Fe{-}CpmMn(CO)_3$ (**5**),
$Cp(CO)_2Fe{-}Cpm(CO)_2Fe{-}BmCr(CO)_3$ (**6**),
$Cr(CO)_3Bm{-}CpmFe(CO)_2CH_2Ph$ (**7**),

where Cp = η^5-C_5H_5, Cpm = η^1:η^5-C_5H_4, Bm = η^1:η^6-C_6H_5.

An X-ray analysis has been performed for a number of such complexes[3–5] confirming that metal carbonyl fragments are bound by the metal-carbon σ-bond. In this paper, we interpreted vibrational spectra of the above-mentioned compounds and studied the mutual electronic influence of each of the metal carbonyl fragments. Carbonyl ligands are known[6] to be suitable spectroscopic indicators for electronic effects.

Experimental

All complexes were prepared according to known procedures[1,2]. IR spectra of CH_2Cl_2 solutions were recorded on a Bruker IFS-25 spectrometer with a resolution of 2 cm^{-1}. A Zeiss cryocell cooled with liquid nitrogen was used for recording the low-temperature spectra of solutions.

Results and Discussion

It is convenient to discuss the spectra of complexes as their structure becomes more complicated. Let us first consider compounds **1** (Fe, Mn) and **2** (Fe, Fe) comparing them to the model mononuclear compounds $Cp(CO)_2Fe(CH)_2Ph$ (**8**) and $CpMn(CO)_3$ (**9**).

For metal carbonyls, the number of νCO bands in the spectra are usually well described on the basis of the local symmetry of each metal carbonyl center $M(CO)_n$.[6] In the case of complex **8**, two modes (*A'* and *A''*) are

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Table 1. Carbonyl stretching frequencies (cm^{-1}) in CH_2Cl_2 solutions

Complex	Fragment		
	$Cp(CO)_nM—$ M = Fe (n = 2) M = Mo, W (n = 3)	$Cpm(CO)_2Fe—$	$CpmMn(CO)_3$ $BmCr(CO)_3$
(Fe) (**8**)	2005, 1948		
(Mn) (**9**)			2035, 1938
(Fe,Mn) (**1**)	2032, 1978		2003, 1916
(Fe,Fe) (**2**)	2029, 1977	1987, 1929	
(Fe,Fe,Mn) (**3**)	2036, 1979	2015, 1956	1999, 1913
(W)*	2038, 1951, 1938		
(W,Fe,Mn) (**5**)	2035, 1965, 1929	2017, 1949	2000, 1922, 1917
(Mo,Fe,Mn) (**4**)	2039, 1963, –	2018, 1947	2000, 1914
(Cr) (**10**)			1971, 1892
(Fe,Fe,Cr) (**6**)	2032, 1980	2018, 1958	1951, 1870
(Fe,Cr) (**7**)		2005, 1951	1966, 1894

* $CpW(CO)_3Br$ in a THF solution.

expected for the local C_s symmetry, in the case of **9**, two modes (A_1 and E) are also expected for the C_{3v} local symmetry. The degenerated E vibrations can be split into two vibrations if the local symmetry is lowered under the influence of other parts of the molecule, for example, polar substituents.

In accordance with this, two νCO bands at 2005 and 1948 cm^{-1} (A' and A'', respectively) (Table 1, Fig. 1, *b*) are observed in the IR spectrum of **8**. Complex **9** also exhibits two νCO bands at 2025 and 1938 cm^{-1} assigned to the symmetrical (A) and degenerated (E) modes, respectively (Fig. 1, *b*).

Four strong bands at 2032, 2003, 1978, and 1916 cm^{-1} are observed in the νCO range of the spectrum of **1** (Fe, Mn) (Fig. 1, *c*), their frequencies being markedly shifted as compared to those in **8** and **9**. The shift can be caused by two major reasons, (i) the vibrational coupling of the CO groups at the different metal atoms, and (ii) the mutual influence of different parts of the molecule. The vibrational coupling does not seem to play any significant role. If the vibrations of the CO groups at different metal atoms were coupled, the number of bands in the spectrum would be determined by the symmetry of the molecule as a whole rather than by the local symmetry of each metal center. In this case, the vibrations of E species of the $Mn(CO)_3$ fragment (C_{3v} symmetry) should be split due to lower symmetry, and thus five νCO bands should be observed in the spectrum.

This is not the case, however, indicating that such coupling is not significant. This is the reason why electron effects are to be considered the main reason for the band shifts. It is easy to assign the bands taking into account that in the spectrum of **8**, the difference between νCO^{sym} and νCO^{asym} for the $Fe(CO)_2$ group is 57 cm^{-1}; in the spectrum of **9**, the difference for the $Mn(CO)_3$ group is 97 cm^{-1}. In the spectrum of **1**, νCO bands can be divided into two groups approximately with the same differences in frequency: 2032 and 1978 cm^{-1} ($\delta\nu$ = 54 cm^{-1}) and 2003 and 1916 cm^{-1} ($\delta\nu$ = 87 cm^{-1}). A rather large width of the 1916 cm^{-1} band, characteristic of degenerated modes in metal carbonyls, proves the assignment of this band to the degenerated E mode of the $Mn(CO)_3$ group. The fre-

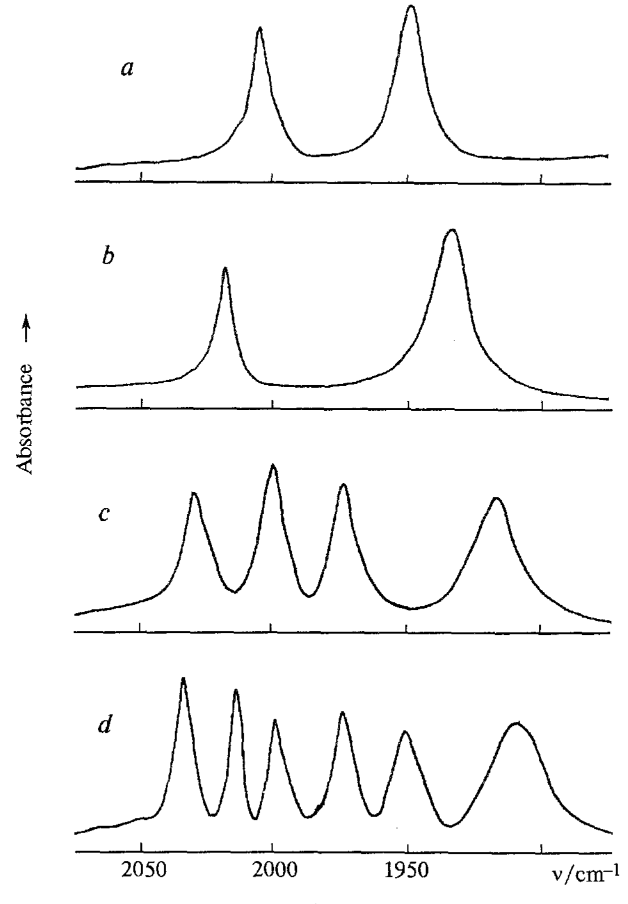

Fig. 1. IR spectra in the νCO region in CH_2Cl_2 solutions: *a*, **8** (Fe); *b*, **9** (Mn); *c*, **1** (Fe,Mn); *d*, **3** (Fe,Fe,Mn).

quencies of the $Mn(CO)_3$ group are down-shifted by 22—32 cm^{-1} as compared to those in **9**. The low-frequency shift indicates that the $CpFe(CO)_2$ group behaves as an electron donating substituent with respect to the $CpmMn(CO)_3$ group. The $CpFe(CO)_2$ substituent is a stronger donor than the NH_2 group, which lowers the νCO frequencies by 13—18 cm^{-1} in a THF solution and by 10—12 cm^{-1} in a cyclohexane solution[7] as compared to unsubstituted cymantrene (CTM). There is no data on aminocymantrene in CH_2Cl_2 solutions but, bearing in mind the band shift under the solvent influence, the νCO bands might be expected in the range 2012—2016 cm^{-1} and 1920—1926 cm^{-1}.

It is known[7] that a νCO value in cymatrene derivatives correlates with the $\sigma_p{}^\circ$ parameter, which is characteristic of the inductive transfer of electronic effects through the metal atom. For NH_2, $\sigma_p{}^\circ = -0.38$; for NMe_2 it is −0.44.[8] The shift values allow the $\sigma_p{}^\circ$ value for the $Cp(CO)_2Fe$ substituent to be estimated as −0.5. Our conclusion is in accord with published data on the inductive constant σ_i of the $Cp(CO)_2Fe$-group, for which the values of −0.13 and −0.25[9,10] were derived from the ^{19}F chemical shifts in the NMR spectra of compounds $FC_6H_5Fe(CO)_2Cp$ indicating that this group belongs to very strong σ-donors.

The bands of the $Cp(CO)_2Fe$ group in the spectrum of **1** are 27—30 cm^{-1} up-shifted as compared to those of **8** indicating that the substituent $C_5H_4Mn(CO)_3$ bound to the iron atom is an electron acceptor, stronger than the $CH_2C_6H_5$ group. It was shown earlier[11] that in compounds of the $CpFe(CO)_2X$ type, the electronic effect is transferred from the substituent X to the carbonyl groups according to the inductive mechanism and that νCO frequencies correlate with the Hammett σ_i constant. Comparison with the data of Ref. 11 prompts the conclusion that νCOs in **1** are close to those for compounds $CpFe(CO)_2X$ where X = C_6H_5 or I. Though in Ref. 11 the spectra were recorded for THF solutions, a σ_i value of 0.4 for the $C_5H_4Mn(CO)_3$ substituent can be approximately evaluated.

With a drop in the temperature, the spectrum of the solution of **1** in CH_2Cl_2 is practically not changed, although at −80 °C, all the bands are 3—4 cm^{-1} down-shifted. The νCO (*E*) band of the $Mn(CO)_3$ group remains broad but its contour becomes slightly asymmetrical, probably due to the degeneracy break-down.

In the spectrum of **2** (Fe, Fe) in a CH_2Cl_2 solution, four bands are also observed, which can be divided into two pairs: 2029, 1977 cm^{-1} ($\delta\nu = 52$ cm^{-1}) and 1987, 1929 cm^{-1} ($\delta\nu = 58$ cm^{-1}) with splitting similar to those observed in the spectrum of **8**. There is reason to conclude that the first pair of bands belongs to the $Cp(CO)_2Fe$ fragment and is shifted to the high frequency range under the influence of the electron withdrawing substituent $C_5H_4(CO)_2FeR$. The shift is approximately the same as for $C_5H_4Mn(CO)_3$, indicating that these substituents are electron acceptors of approximately the same strength. The frequencies of the $C_5H_4(CO)_2FeR$ fragment are down-shifted under the influence of the electron donor substituent $Cp(CO)_2Fe$ and the low-frequency shift (18—19 cm^{-1}) is compatible to that in **1**.

In the spectrum of complex **3** (Fe, Fe, Mn) (Fig. 1, *d*), there are six νCO bands, as could be expected. Taking into consideration the band assignment in the spectra of **1** and **2**, the band assignment for **3** is straightforward.

The bands at 2036 and 1989 cm^{-1} belong to the "upper step" of the staircase ($Cp(CO)_2Fe$—), the bands 1999 and 1913 cm^{-1} belong to the "lower step" of the staircase (—$C_5H_4Mn(CO)_3$), and the bands 2015 and 1956 cm^{-1} belong to the "middle step" (—$C_5H_4(CO)_2Fe$—). The frequencies of $Mn(CO)_3$ are close to those in **1** but are 3—4 cm^{-1} lower due to an additional influence of the second electron-donating iron carbonyl group. The additional shift is not large, which means that the influence drops rather fast with an increase in the number of steps. The frequencies of the terminal $Cp(CO)_2Fe$ group are close to those in **2**, though they are somewhat higher due to the total electron-withdrawing effect of two metal carbonyl groups. The frequencies of the central step are also somewhat higher as compared to those for **2** but the shift (8—10 cm^{-1}) is markedly less than in **2**; which may be accounted for a partial compensation of the acceptor effect of the $C_5H_4Mn(CO)_3$ group by the donor effect of the $Cp(CO)_2Fe$ group. When the temperature is lowered to −70 °C, no changes are observed in the spectrum of **3** as well as in the spectrum of **1**. Only a low-frequency shift by 2—3 cm^{-1} is observed, and the νCO (*E*) band of the $Mn(CO)_3$ fragment becomes asymmetrical.

For compounds **4** and **5**, the spectral picture in the νCO range is more complicated. In complexes of the $CpM(CO)_3X$ type (M = Mo, W), as a rule, the local C_{3v} symmetry does not hold and 3 νCO bands are observed[12]. For complexes **4** and **5**, broad bands with poorly resolved maxima are observed in the range of 1900—2200 cm^{-1}; the band contours for **4** and **5** are different. However, the bands of the central fragment $Fe(CO)_2$ and the fragment $Mn(CO)_3$ are easily recognized because their frequencies coincide with the corresponding frequencies in **3**, pointing to the similarity of electron donating properties of the $Cp(CO)_2Fe$, $Cp(CO)_3Mo$, $Cp(CO)_3W$ groups. The other bands at 2035, 1965, and 1929 cm^{-1} in the spectrum of **5** are close to those observed in the spectrum of $Cp(CO)_3WBr$. In the spectrum of **4**, only two bands of the $Mo(CO)_3$ group are observed. The third band is lacking, probably due to the overlap with νCO of $Mn(CO)_3$, which is asymmetrical from the high-frequency side. It is remarkable that the high-frequency parts of the spectra **4** and **5** are much the same; in the range below 2000 cm^{-1}, frequency values are close but the intensity ratio is quite different. Such a difference may be caused by rotational isomerism, which will be discussed in our next paper.

In complex **6** (Fe, Fe, Cr), frequencies of both $Fe(CO)_2$ fragments are close to the corresponding frequencies in the spectrum of **3** (Fe, Fe, Mn) thus suggesting similar electron acceptor properties of the $CpmMn(CO)_3$ and $BmCr(CO)_3$ groups. The frequencies of the $Cr(CO)_3$ group in **6** are 20—22 cm^{-1} lower as compared to those for $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ (**10**) due to the donor effect of the other part of the molecule.

The analysis of the spectra of **1—6** in the νCO range therefore allows the conclusion to be drawn that the vibrational coupling between metal carbonyl centers does not sufficiently affect the band positions. In the case of complex **7**, however, where two fragments $BmCr(CO)_3$ and $Cpm(CO)_2FeCH_2Ph$ are linked not by the metal atom but by the C—C σ-bond between two organic ligands, there are two pairs of νCO bands at 2005, 1951 cm^{-1} and 1966, 1894 cm^{-1}. The first pair virtually coincides with νCOs in **8**, and the second — with νCOs in **10**. That means that the electronic effect is not practically transferred through the system of σ-bonds between the organic parts of the molecule. Unlike **7** and $Cp(CO)_2WCH_3PPh_2\text{—}CpmFe(CO)_2Me$ with the P—C σ-bond[13], compounds **1—6** can be considered a system of mutually affecting substituents, $Cp(CO)_nM$ substituents bound to the π-ring through the metal atom being strong electron donors and $(\eta^1,\eta^n\text{-}C_nH_{n-1})M(CO)_3$ ($M = Mn$, $n = 5$; $M = Cr$, $n = 6$) substituents bound through the carbon atom of the ring being strong electron acceptors.

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