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NMR studies of mononuclear $(CH_3)_nCpM(CO)_3^-Na^+$ and dimeric $[(CH_3)_nCpM(CO)_2]_2$ complexes

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Abstract

The ^1H, ^{13}C and ^{17}O NMR spectra of the mononuclear $(CH_3)_nCpM(CO)_3^-Na^+$ ($Cp = C_5H_{5-n}$; $n = 0$, 3–5) complexes and ^1H and ^{13}C NMR spectra of dimeric $[(CH_3)_nCpM(CO)_2]_2$ ($n = 0$, 1, 3–5; M = Cr, Mo, W) complexes indicate that the data for C(CO) groups in the two complexes obey the "triad effect" and tend to shift downfield with growth of *n*. These observations imply that the electron interaction of the CO groups in the series $[(CH_3)_nCpM(CO)_2]_2$ (M = Cr, Mo, W) are qualitatively very similar and fail to reflect the linear crystalline structure of $[CpMo(CO)_2]$.

Introduction

The differences in the chemistry [1–3] and the crystal structures [4–7] between the dimeric cyclopentadienyldicarbonyl complexes of Cr and Mo have gained the interest of a number of researchers [6,8,9]. Some authors ascribe these differences to steric [4,9], whereas others ascribe them to electronic [6] interactions.

We have suggested that the real reason for these differences can be revealed by using a Cp ligand in which different numbers of methyl groups are present, so that the electronic and steric characteristics of the ligand are changed to varying degrees. This investigation was supplemented by the data from the ^{13}C NMR spectra of the unsubstituted derivatives, $[CpM(CO)_2]_2$ (M = Mo or W) reported in ref. 10. The "triad effect", which had been established previously for arenecarbonyl derivatives

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of Cr, Mo and W [11], as well as the ^{13}C NMR data already mentioned suggest the existence of different electronic interactions of the CO groups with the M≡M fragment.

Results and discussion

$(CH_3)_nCpM(CO)_3^-\ Na^+$ ($M = Cr, Mo, W$; $n = 0, 3–5$)

In order to ascertain whether the "'triad effect" also holds for the cyclopentadienyl carbonyl complexes of Cr, Mo and W, we first synthesized the methyl homologues of mononuclear complexes $Me_nCpM(CO)_3^-\ Na^+$ (Me = CH$_3$; $n = 0$, 3–5; M = Cr, Mo, W) and then studied their ^{1}H, ^{13}C and ^{17}O NMR spectra. In Table 1 are listed the chemical shifts for the magnetic nuclei of the $Me_nCpM(CO)_3^-$ anions (M = Cr, Mo, W). It follows that as the degree of Cp ring substitution increases the variations in the shielding of the magnetic nuclei in the Me$_n$Cp fragment begin to resemble the neutral cyclopentadienyl-di- and -tri-carbonyl complexes of Re, Co, Mn and Rh [12–14] previously investigated. Thus the shielding of most of the nuclei in the Me$_n$Cp fragment increases and the introduction of a methyl group into the vicinal position in respect of the former group results in a successive upfield shift of the signals from the C(CH$_3$) group by 1.7 to 1.8 ppm.

Deshielding of ^{13}C(CO) and ^{95}Mo nucleus is also observed in the M(CO)$_3$ and Mo(CO)$_3$ fragments, respectively. Similar deshielding of ^{13}C nuclei with growing methyl substitution is also observed for cyclopentadienyl-di- and -tri-carbonyl [12–14] and arenetricarbonyl [16] complexes of transition metals, and is found to be due to growing dative interaction ($Md \rightarrow \pi^*$(CO)).

However, in contrast to the neutral complexes [12–14] deshielding of ^{17}O(CO) is observed in $Me_nCpM(CO)_3^-$ anions with increase in n. The deviation in this case

Table 1

^{13}C, ^{17}O (and ^{95}Mo) chemical shifts (ppm) for [Me$_n$CpM(CO)$_3$]Na (n = 0, 3–5; M = Cr, Mo, W) in THF relative to TMS and H$_2$O

M	n	δ(O(CO))	δ(C(CO))	δ(C$_{key}$)	δ(C(CH))	δ(C(CH$_3$))	δ(Mo) [b]
Cr	0	366.3	247.72	–	82.87	–	
Cr	4	371.1	248.97	96.57	81.64	14.10	
				95.96		12.10	
Cr	5	372.2	249.17	95.28	–	12.08	
Mo	0	353.4	237.18	–	87.06	–	−2123
Mo	3	353.8	238.77	103.67(1) [a]	87.48	15.92(1)	−1985
				103.20(2)		14.01(2)	
Mo	4	354.6	239.42	102.04	85.43	14.34	−1946
				101.80		12.38	
Mo	5	354.9	239.97	100.11	–	12.25	−1900
W	0	339.9	227.99	–	85.38	–	
W	4	344.7	231.27	100.78	84.31	14.10	
				100.31		12.25	
W	5	345.2	231.83	99.55	–	12.18	

[a] Relative intensities in parentheses. [b] Relative to Na$_2$MoO$_4$ upfield.

can most probably be ascribed to a specific Na...O(CO) interaction in each ion pair.

It is seen from the chemical shifts of the C(CO) groups in the series $Me_nCpM(CO)_3^-$ (M = Cr, Mo, W), that the C(CO) shielding values in the corresponding homologues increase by 10 to 12 ppm for each metal atom replacement in the sequence Cr → Mo → W, which means that the "triad effect" holds true for the $Me_nCpM(CO)_3^-$ anion series as well as for the $M(CO)_6$ series and the arenetricarbonyls of Cr, Mo and W. This implies that the electron interactions involving CO groups in this type of complexes are quantitatively similar (e.g. in the $Me_nCpM(CO)_3^-$ anion series).

$[Me_nCpM(CO)_2]_2$ (M = Cr, Mo. W; $n = 0$, 3–5)

Let us consider ^1H and ^{13}C NMR data for homologous series of dimeric complexes $[Me_nCpM(CO)_2]_2$ (M = Cr, Mo, W; $n = 0$, 3–5) listed in Tables 2 and 3. Chemical shifts of C(CO) indicate that their resonance signals are much more downfield than the C(CO) signals in the corresponding hexacarbonyls of Cr, Mo and W, indicating that their CO group is non-terminal. In fact, the chemical shifts, δ(C(CO)), for the neutral cyclopentadienylcarbonyl complexes of most transition

Table 2

^{13}C chemical shifts (ppm) in $[Me_nCpM(CO)_2]_2$ (M = Cr, Mo, W; $n = 0$, 3–5) complexes in respect to TMS

M	n	δ(C(CO))	$\delta(C_{key})$	δ(C(CH))	δ $C(CH_3)$	Solvent [c]
Cr	0	249.0	–	91.10	–	B
Cr	3	250.70	103.16(2)	91.39	13.00(1)	B
			103.10(1)		11.18(2)	
Cr	4	250.92	101.61	90.25	11.90	B
			101.25		9.45	
Cr	5	251.20	100.20	–	9.60	B
Mo	0	236.70	–	92.24	–	A
		236.68	–	92.54	–	C
Mo	1	236.77	109.16	93.11	13.20	C
				89.84		
Mo	3	237.88	106.44(2) [a]	92.50	13.20(1)	B
			104.71(1)		11.44(2)	
Mo	4	238.22	106.10	89.31	11.70	B
			103.54		9.82	
Mo	5	238.78	103.13	–	9.86	B
		239.31	103.48	–	9.99	C
Mo	Bu^t [b]	238.90	129.80	91.90		C
				90.60		
W	0	223.42	–	92.43	–	C
W	3	224.13	105.59(2)	91.86	12.90(1)	C
			104.43(1)		11.16(2)	
W	4	225.30	105.30	89.60	11.80	C
			103.50		10.00	
W	5	225.38	102.45	–	10.00	B

[a] Relative intensities in parentheses. [b] $Bu^t = [(CH_3)_3CCpMo(CO)_2]_2$. [c] A in C_6D_6, B in $CDCl_3$, C in CD_2Cl_2.

Table 3

Stretching C≡O vibrations (ν) and proton chemical shifts (ppm) for the complexes $[Me_nCpM(CO)_2]_2$ (M = Cr, Mo, W; n = 0, 3–5)

M	n	ν(C≡O) (cm^{-1})	δ(H(Cp))	δ(H(CH$_3$))	
Cr	0	1900, 1880	4.820		–
Cr	3	1875, 1853	4.226	1.957(1) [a]	1.842(2)
Cr	4	1872, 1848	4.304	1.882	1.742
Cr	5	1875, 1857	–		1.734
Mo	0	1889, 1859	5.236		–
Mo	1	1887, 1840	4.975		1.938
Mo	3	1881, 1841	4.906	1.951(1)	1.930(2)
Mo	4	1876, 1838	4.790	1.922	1.916
Mo	5	1874, 1846	–		1.914
W	0	1885, 1830	4.780		–
W	3	1881, 1823	4.301	2.096(1)	2.070(2)
W	4	1879, 1821	4.297	2.071	2.029
W	5	1875, 1828	–		2.021

[a] Relative intensities in parentheses.

metals are close to δ(C(CO)) for the corresponding carbonyls [11,16]. On the other hand, it is unlikely that the downfield δ(C(CO)) shifts observed for the $[Me_nCpM(CO)_2]_2$ complexes are due to an electron density transfer from the Me_nCp fragment to C(CO) within the $Me_nCpM(CO)_2$ fragment. For example, signals from C(CO) appear either in a stronger field than, or in the same region as, those from the mononuclear anions $Me_nCpM(CO)_3^-Na^+$ (Table 1), in which the transfer of electron density to antibonding orbitals of the CO group by M$d \rightarrow \pi^*$(CO) interaction (regarded as a measure of the downfield-shift of the C(CO) signal) should be higher than in the corresponding dimeric complexes. This is also true for $Me_nC_6H_{6-n}M(CO)_3$ (n = 0–6; M = Cr, Mo, W) where δ(CO) varies in the range of 235 to 211 ppm depending on n and the nature of M. It is natural to assume that the presence of a single positive charge on the metal atom in dimeric complexes should result in a lowered metal-atom d-electron acceptor ability by the CO groups than in the case of arene complexes with zero-valent atoms, and the signal of C(CO) in dimers should be more shielded. However, the picture observed is just the reverse (Table 2).

In the ^{13}C NMR spectra of $[Me_nCpM(CO)_2]_2$, the resonance signals of the CO groups bonded to the M≡M fragment are shifted downfield from the resonance signal of C(CO) in the corresponding carbonyls by 30–40 ppm. It follows from these considerations that a CO group in dimeric complexes $[Me_nCpM(CO)_2]_2$ (M = Cr, Mo, W) is most probably involved in the additional (in respect of terminal CO) interaction with another metal atom thus leading to deshielding or its becoming susceptible to the downfield influence of the M≡M bond anisotropy [17,18]. Stretching vibration frequencies of the C≡O bond (Table 3) and the tilt of CO groups with respect to the M≡M bond [4,7,19] indicate that the CO groups are probably involved in a semibridging interaction with the second metal atom [6,8]. At present, the available IR and ^{13}C NMR data unambiguously confirm the nature of semi-bridging interaction since donation of π-electrons from the C≡O bond to the second metal atom and return acceptance of π-electrons from M (or from the M≡M bond) by a π^*-orbital of CO reported previously [5,6,8,9] should result in similar changes in the NMR (δ) and IR (ν) parameters.

In the ^{13}C NMR and IR spectra (CO region) of the dimeric complexes under study, deshielding of the C(CO) and a decrease in the frequencies of the stretching vibrations (ν) of the C≡O bond is observed with an increase in the degree of substitution in the Cp ring (Tables 2 and 3) which is similar to the mononuclear cyclopentadienyl carbonyl complexes [12,14]. Thus these changes are superficially similar to those of ν(C≡O) and δ(C(CO)) due to growing dative M$d \rightarrow \pi^*$(CO) interaction [11,12]. If the downfield shift C(CO) were in fact due to semi-bridging interactions alone, an upfield shift of the C(CO) signal with growing n was to be expected since a decrease in the semi-bridging interaction is likely. A progressive increase in the length of the M≡M bond and the mean angle (angle C(1,2)M′) of CO tilt in respect of the M≡M bond, with increase in n is observed in $[Me_nCpM(CO)_2]_2$ complexes (M = Cr; $n = 0, 3, 5$) [4,6,19] and M = Mo; $n = 0, 5$) [5,7] with established structures. This results in a lengthening of the M′...C(1,2) contacts and thus in a lower semi-bridging interaction, which should then lead to upfield shifts of the C(CO) signals. The changes in ν and δ with growing n are inverse and are consistent with an increasing M$d \rightarrow \pi^*$(CO) interaction.

Although comparative evaluation of $\delta(^{13}$C(CO)) values in $[Me_nCpM(CO)_2]_2$ complexes leads to a generally accepted assumption on the presence of a semi-bridging CO group, nevertheless, the variation of $\delta(^{13}$C(CO)) with n is indicative of C(CO) shielding being determined by the CO group M$d \rightarrow \pi^*$(CO) interaction with its "own" M atom.

The ^{17}O NMR chemical shifts for the $[Me_nCpMo(CO)_2]_2$ complexes ($n = 0, 4, 5$) of 424.3, 424.0 and 421.6 (this work) ppm, respectively, are also correlated to the increase in Mo$d \rightarrow \pi^*$(CO) [11,12]. In fact, a comparatively downfield shift of $\delta(^{17}$O) (as compared to $\delta(^{17}$O) in $Mo(CO)_6$ and $CpMo(CO)_3^-$, which have $\delta(^{17}$O) of about 365 and 353 ppm, respectively ref. 11 and Table 1) supports the assumption on O(CO) deshielding, and the emergence of a semi-bridging π(CO)$\rightarrow d$ M interaction. Furthermore the increase in the C(1,2)MoMo′ angle with increase in n is accompanied by the predicted upfield shift (424 ppm → 421 ppm) of the ^{17}O(CO) signal. However, the downfield of the C(CO) shift signal (with increase in n) is not consistent with our assumption. In addition the $\delta(^{17}$O(CO)) value of 400 ppm for $[CpMo(CO)_3]_2$ [25,26], which has only terminal CO groups, most probably eliminates the possibility of this π(CO)$\rightarrow d$M interaction.

The chemical shifts for the C(CO) groups in the series $[Me_nCpM(CO)_2]_2$ ($n = 0$, 1, 3–5; M = Cr, Mo, W) (Table 2), depending on the nature of the metal indicate that the "triad effect" also holds true for them, which is why the electronic interactions involving the CO groups are qualitatively very similar in the three homologous series. This implies that either the $[CpMo(CO)_2]_2$ complex is bent in solution, similar to $[Me_5CpMo(CO)_2]_2$ and to the chromium complexes or the linear structure of $[CpMo(CO)_2]_2$ has no effect on the electronic interactions of CO groups ($n = 0$), in comparison to the bent complexes.

Studies on the photoelectron spectra of $[CpM(CO)_2]_2$ (M = Cr, Mo, W) complexes in the gas phase [9] similarly revealed no appreciable changes in the electron structure of these three species. The ^{13}C NMR spectra of the $[Me_nCpM(CO)_2]_2$ complexes in the crystalline state could provide useful information. The ^{13}C NMR data for $[CpMo(CO)_2]_2$ in solution have been reported [10]. The resonance signal from the C(CO) occurred in a rather strong field (δ 195.9 ppm). Upfield signals of C(CO) were also obtained [20,21] for the $[Me_nCpM(CO)_2]_2$ complex ($n = 0$, 1, 3–5; δ 206–204 ppm). Since the "triad effect" was found to be untrue for the $[Me_nCpM(CO)_2]_2$ (M = Cr, Mo, W) complexes, in this case and a reverse trend in the variation of δ(C(CO)) in the $[Me_nCpMo(CO)_2]_2$ series was observed with the growth of n, and it was concluded that very different electronic interactions by the CO groups are present in the $[Me_nCpMo(CO)_2]_2$ complexes as compared to $[Me_nCpM(CO)_2]_2$ (M = Cr, W). It is shown in this study that these upfield signals of C(CO) in the $[Me_nCpMo(CO)_2]_2$ ($n = 0$, 1, 3–5) complexes were due to signals from the C(CO) folding back into the spectrum.

The $Me_nCpM(CO)_3Na$ and $[Me_nCpM(CO)_2]_2$ complexes were prepared by published procedure [22–24]. The ^1H, ^{13}C and ^{17}O NMR spectra were recorded on a Bruker-WP-200 SY NMR spectrometer operating at 200.13, 50.31 and 27.13 MHz, respectively.

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