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^{1}H, ^{13}C, ^{17}O NMR and IR (CO-region) spectroscopic and mass-spectrometric studies of Me$_n$CpM(CO)$_2$ (M = Co, Rh) homologs

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Abstract

On the basis of ^{1}H, ^{13}C, ^{17}O NMR and IR (CO-region) spectroscospic studies of Me$_n$CpM(CO)$_2$ (M = Co, Rh; n = 0–5; Me = CH_3), common trends and differences in the changes of ^{1}H and ^{13}C chemical shifts have been established for Me$_n$CpM(CO)$_x$ (x = 2, M = Co, Rh; x = 3, M = Mn, Re) and possible reasons for this are discussed. The values of $J(^{103}\text{Rh}-^{13}\text{C})$ in the Me$_n$CpRh(CO)$_2$ series support the suggestions. In the mass spectra of Me$_n$CpM(CO)$_2$, the molecular ions (M^+) undergo successive CO abstractions. The dehydrogenation that follows gives fulvene-like ions. The presence of one or more Me groups in the Cp ring does not significantly effect the intensities (J) of M^+, which is regarded as the involvement of metal orbitals of various symmetries in a π-interaction with Cp and CO.

Introduction

The factors responsible for resonance signal upfield shifts of C(Cp) resonances under coordination of Me$_n$Cp$^-$ anions to transition metal atoms [1–4] are as yet unclear [2–4], but ^{1}H and ^{13}C NMR spectroscopy of their methyl homologs are beginning to provide some answers. Studies on Me$_n$CpM(CO)$_3$ (M = Mn; Re; n = 0–5) [5,6] in which CO was used as auxiliary indicator group showed that where a Me group was substituted for H, the changes in the shielding of the substituted C(key) and α-(C(2.5)) carbon atoms in the Cp ring could be interpreted in terms of redistribution of π-electron density over the Cp fragment under the action of the Me group. A ^{1}H and ^{13}C NMR study of (Me$_n$Cp)$_2$M (M = Fe, Co$^+$; n = 0–5) [7,8] revealed that shielding of the C(Me) groups in the Cp ring was caused by steric

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interaction of the vicinal Me groups. However, no reports have been published on the effect of electronic and structural features of a ML_x fragment (L = Cp, $x = 1$; L = CO, $x = 2$–3) on the shielding of magnetic nuclei of Cp. In the NMR spectra of the $Me_nCpRh(CO)_2$ complexes, the possibility to observe the spin–spin interaction of the ^{103}Rh atom with C(Cp) and C(CO) provides an additional channel of information on the interaction of a transition metal atom with a Cp ring. Since a number of X-ray diffraction studies [9 12] have appeared in recent years, clearly defining the effect of an ML_x fragment (L = CO, M = Mn, Re, $x = 3$; M = Co, Rh, $x = 2$) on the electron density distribution over the Cp ring with the crystalline state of $R_5CpM(CO)_x$, it seemed expedient to examine $Me_nCpM(CO)_2$ (M = Co, Rh) by use of NMR techniques and to compare the results with those for $Me_nCpM(CO)_3$ (M = Mn, Re).

Results and discussion

1. NMR spectra of $Me_nCpM(CO)_2$ (M = Co, Rh)

Tables 1 and 2 show ^1H and ^{13}C chemical shifts of Me_nCp ligands coordinated with a $M(CO)_2$ (M = Co, Rh) fragment. From the tables it can be seen that the resonance signals of the H(Cp) ring tend to shift upfield as observed in the $Me_nCpM(CO)_3$ (M = Mn, Re) [5,6] and $(Me_nCp)_2M$ (M = Fe, Co^+) series [7,8]. Since anisotropy of the C–Me bond fails to change H(Cp) shielding [13], the observed changes can be traced to the redistribution of electron density over the Cp ring under the effect of Me groups. The signals from the H(Me) in di- and tri-carbonyl complexes unlike those in sandwich complexes [7,8] exhibit non-monotonous upfield shift. In the 1,2,4-Me_3Cp derivatives, resonance signals of the protons in vicinal Me groups are more downfield than those of single Me groups (Tables 1 and 2). Owing to anisotropy of the C–Me bond, the proton signals from vicinal groups were generally about 0.1 ppm more upfield than those of single Me groups [7,8]. The difference in H(Me) shielding observed in carbonyl complexes is probably due to the magnetic anisotropy of the $M(CO)_x$ fragment ($x = 2$, 3) [14].

Table 1

^1H and ^{13}C chemical shifts of the $(CH_3)_nCp$ fragment in $(CH_3)_nCpCo(CO)_2$ homologs in $CDCl_3$ ($n = 0$–5) relative to TMS

n	^{13}C [a]			^1H [a]	
	C(key)	*C*(CH)	*C*(Me)	*H*(Cp)	*H*(Me)
0	–	84.55	–	5.044	–
		82.79		5.021	
1	101.62	86.14	13.756	4.853	1.927
		87.81 (1)			
2	100.05	83.79 (2)	13.717	4.901	1.910
3	99.91 (1)	86.41	13.461 (1)	4.875	1.893 (2)
	96.32 (2)		12.044 (2)		1.772 (1)
4	99.30	83.88	12.157	4.861	1.876
	96.00		10.735		
5	96.71	–	10.537	–	1.608

[a] ( ) = relative intensity.

Table 2

^{1}H and ^{13}C chemical shifts of $(CH_3)_nCp$ fragment in $(CH_3)_nCpRh(CO)_2$ homologs in $CDCl_3$ (n = 0–5) relative to TMS

n	^{13}C ^{a}			^{1}H ^{a}	
	C(key)	*C*(CH)	*C*(Me)	*H*(Cp)	*H*(Me)
0	–	87.76[3.5]	–	5.463	
1	106.03[3.2]	89.54[3.8]	14.12	5.257	2.068
		87.75[3.5]			4.859
2	105.42[3.3]	89.76[3.8]	13.56	5.134	2.054
		85.25[3.5]			
3	99.87[3.4]	89.78[3.5]	13.900 (1)	5.028	2.041(2)
	103.77[3.3]		12.400 (2)		1.996 (1)
4	102.14[3.3]	87.82[3.8]	12.520	4.985	2.024
	100.87[3.4]		10.980		
5	100.93[3.4]	–	10.895	–	2.016

[a] ( ) = relative intensity, [ ] = coupling constant ^{103}Rh–^{13}C(Cp) in Hz.

However, no difference in the shielding of the ^{13}C(Me) groups of the Me$_n$Cp fragment, was observed with increase in n.

We support the suggestion that the changes in the shielding of the ^{13}C nuclei of the aromatic ring and the substituents are mostly determined by the variations in the paramagnetic component of the chemical shift (σ_p) in accord with previous studies on arene- and cyclopentadienyl-carbonyl complexes of transition metals. In the case of a Me substituent only slightly disturbing the electron system of a CpM fragment, the mean values $\langle r_{2p}^{-3} \rangle$ [15] is regarded as the dominant σ_p variant.

Tables 1 and 2 set out the variation in the shielding of the carbon nuclei of the Cp ring in the Me$_n$CpM(CO)$_2$ (M = Co, Rh) complexes in which H(Cp) was replaced by Me groups to give complexes similar to the methyl analogs of Cp_2M (M = Fe, $\overset{+}{\mathrm{Co}}$) [7,8] and $CpM(CO)_3$ (M = Mn, Re) [5,6] previously investigated: viz. (i) As the number of methyl groups grows, the signals of most of the carbon nuclei tend to shift upfield. (ii) The introduction of the first Me group into the Cp ring results in a strong (17–18 ppm) downfield shift of the substituted carbon signal. (iii) Me group in the vicinal position tends to shift the resonance signal of the previous Me group upfield by about 1.6 ppm. The spin–spin interaction constant ^1J(C–H(Cp)) is reduced.

Along with the similarities, however, there are some differences. One distinction is that in the $CpM(CO)_3$ series (M = Mn, Re) there is a different tendency for shielding of the α-C(C(2,5)) carbons of Cp where the first methyl group appears in Cp. While α-C(C(2,5)) are shielded in MeCpM(CO)$_3$ (M = Mn, Re) [5,6], they are deshielded in MeCpM(CO)$_2$ (M = Co, Rh). On the traditional concepts [1,5–8,13] on the redistribution of the electron density over a Cp ring due to introduction of a methyl group, shielding of the αC(C(2,5)) should be expected in the resulting MeCp fragment. This approach has been interpreted [32] by which π-electron system perturbation due to methyl substituent is partially caused by electron density transfer from Me group but mainly by polarisation of the π electron system. From this point of view the charge reorganisation in the Cp ligand of $CpM(CO)_3$ and $CpM(CO)_2$ complexes as a result of adequate perturbation by the Me group occurs with some variation. On the basis of a previously published report [32], this phenomenon might be interpreted in terms changes of the sign of the mixing coefficients of the original ligand wave functions. This in turn may have been the result of splitting of energy level positions because of differences in the symmetry and electron structure of the $M(CO)_x$ fragments ($x = 2$, M-d^8, $x = 3$, M-d^6). It should be noted that these data are consistent with the X-ray studies carried out previously [9–12]. When the Cp ring is coordinated with a $M(CO)_3$ (M = Mn, Re, d^6) fragment, the Cp ring experiences "diene" distortion, but when Me_5Cp is coordinated with $M(CO)_2$ (M = Co, Rh, d^8) the Cp ring displays "allyl-ene" distortion [11,12].

The bonding of the Me_5Cp ring with a $M(CO)_2$ fragment is distinctive in that C(2,5) atoms of the ring are somewhat closer to M than C(1,3,4), i.e. they are more strongly bonded to $M(CO)_2$. This distortion is not observed in the NMR spectra of the completely substituted or unsubstituted Co and Rh derivatives (Table 1 and 2); however, the introduction of the first Me group into the unsubstituted Cp ring should enhance this distinction [17].

The changes in the spin–spin interaction of the ^{103}Rh atom with the ring carbons (Table 2) on introducing a Me group further confirms the above. The $J(^{103}Rh–^{13}C(Cp))$ spin–spin interaction constant in unsubstituted $CpRh(CO)_2$ was found to be 3.5 Hz. In monosubstituted $MeCpRh(CO)_2$, the coupling constants of $J(^{103}Rh–^{13}C(key))$, $J(^{103}Rh–^{13}C(2,5))$ and $J(^{103}Rh–C(3,4))$ are 3.2, 3.8 and 3.5 Hz, respectively.

This implies that the electron population of the e_1-symmetry orbitals influenced by a Me group with the resulting electron density being accepted by a $M(CO)_2$ fragment, predominantly on α-(C(2,5)), is probably responsible for the downfield shift of the resonance signal α-C(C(2,5)) in $MeCpM(CO)_2$ as compared to C(Cp) in an unsubstituted Cp ring of $CpM(CO)_2$ (M = Co, Rh).

The above evidence (electron action of a Me group and the distribution of electron density over a Cp ring caused by a $M(CO)_2$ fragment) falls short in providing an answer to the variation of the shielding of α-C in the MeCp fragment in our systems and that in other systems [1,5]. For example, within the framework of the above factors it is difficult to understand why deshielding of about 1.8 ppm of α-C(C(2,5)) occurs in monomethyl ferrocene [1] and in the $MeCp^-$ anion [5]. If the magnetic anisotropy of the C–Me bond is regarded in the light of the expression [18]:

$$\Delta\sigma = \Delta\chi(1 - 3\cos^2\theta)/12\pi R^3,$$

where $\Delta\chi$ is polarizability of the C–Me bond equal to 140×10^{-36} m^3/molecule [19], θ is 36° and R is 0.2 nm, a downfield shift of about 0.35 ppm for α-C(C(2,)) which is rather far from the observed value of 1.8 ppm is observed. The replacement of the H(Cp) ring by a methyl group[*] causes a steric perturbation of α-C(C(2,5)) resulting in a minor paramagnetic contribution to shielding.

Consequently, the stronger the bond between the π-electrons of Cp with the carbon skeleton of the ring, the lower will be the downfield shift that is expected during substitution. For example, α-C(C(2,5)) is not significantly deshielded in the

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[*] The separation of this carbon atom from α-C(C(2,5)) is 2.65 Å, which is far shorter than the sum of the Van der Waals radii [20].

cation of 1,1′-dimethyl cobalticinium [8] (where the Co atom is an oxidation state of +3) while deshielding of about 1.8 ppm is observed in 1,1′-dimethylferrocene (Fe^{2+}) and in the $MeCp^-$ anion [5].

^{13}C and ^{17}O chemical shifts of CO groups

It can be seen from the stretching vibration frequencies of the C≡O bond in the $Me_nCpM(CO)_2$ complexes (see Table 3) that the tendency for $\nu(C{\equiv}O)$ to vary, as observed previously in mononuclear cyclopentadienyl tricarbonyl homologs of Mn and Re ($Me_nCpM(CO)_3$) [5,6], also exists in the two series under study. This tendency was interpreted [5,6] as the growth of the dative $Md \rightarrow \pi^{\star}(CO)$ interaction due to destabilization of the metal *d*-orbitals by methyl groups. In the NMR spectra, this was accompanied by the deshielding of the $^{13}C(CO)$ group and by the shielding of the $^{17}O(CO)$ group, since this tends to exercise an antibonding effect on one of the π-components of the C≡O bond [15]. It follows from Table 3 that these trends in ^{13}C and $^{17}O(CO)$ chemical shifts are also observed in Co and Rh complexes. In contrast to the analogous series previously studied, the presence of spin–spin interaction between the ^{103}Rh atom and $^{13}C(CO)$ allows us to use it as an additional criterion in favor of the $Md \rightarrow \pi^{\star}(CO)$ interaction suggested above. It is seen from Table 3 that $J(^{103}Rh{-}^{13}C(CO))$ tends to grow monotonously, if only slightly, with increase in number of methyl substituents in the Cp ring, which supports the idea of an increasingly dative $Md \rightarrow \pi^{\star}(CO)$ interaction as n increases consistent with the synergism of σ- and π-components of the M–C(CO) bonds. That the differing degrees in shielding of the ^{13}C and $^{17}O(CO)$ nuclei depends on the nature of the metal atom (M = Co, Rh) resembles that observed in NMR studies of $Me_nCpM(CO)_3$ (M = Mn, Re): in the derivatives of the transition metals of the first row the electron effect of the substituents is mainly localized on O(CO).

Mass spectra of $Me_nCpM(CO)$ (M = Co, Rh)

Mass spectrometry of $Me_nCpM(CO)_3$ (M = Mn, Re) [21,22] revealed significantly different fragmentations of their molecular ions (M^+). While Mn–$CpMe_n$ bond-breaking was typical for Mn derivatives after decarbonylation, those of Re indicated intensive dehydrogenation of Me groups in fragment ions $(M-2CO)^+$ $(n > 1)$.

Table 3

^{13}C and ^{17}O chemical shifts of CO groups and frequencies of stretching vibrations of the C≡O bond in $Me_nCpM(CO)_2$ complexes (M = Co, Rh; n = 0–5)

n	M = Co				M = Rh [a]			
	δ (ppm)		ν (cm^{-1})		δ (ppm)		ν (cm^{-1})	
	$^{13}C(CO)$	$^{17}O(CO)$			$^{13}C(CO)$	$^{17}O(CO)$		
0	204.72	361.58	2035	1975	191.30	347.34	2054	1990
1	205.29	358.10	2028	1968	191.96	346.85	2050	1986
2	206.33	355.04	2022	1962	192.53	346.00	2046	1984
3	206.88	253.71	2025	1965	193.06	345.10	2044	1980
4	207.23	353.21	2021	1961	193.74	344.29	2039	1976
5	207.90	352.99	2016	1965	194.29	343.14	2037	1971

[a] $J(^{103}Rh{-}^{13}C(CO)$83.1 Hz, $n = 0$; 85.0 Hz $n = 5$.

Table 4

Intensities (as total ion current) of Co-containing ions in the mass spectra of $(\mathrm{CH_3})_n\mathrm{CpCo(CO)_2}$ (n = 0–5, 70 eV)

Ions	n					
	5	4	3	2	1	0
M^+	9.9	9.0	10.2	9.2	10.2	7.6
$(M-\mathrm{CO})^+$	11.3	12.2	12.7	11.2	12.4	8.1
$(M-2\mathrm{CO})^+$	32.4	32.9	33.0	31.9	32.4	34.8
$(\mathrm{CoL}-\mathrm{H})^{+\,a}$	5.0	4.0	4.8	9.8	18.8	–
$(\mathrm{CoL}-2\mathrm{H})^+$	27.2	23.4	21.0	14.8	2.2	–
$(\mathrm{C_3H_3Co})^+$	–	–	–	–	1.2	8.7
$(\mathrm{C_3H_2Co})^+$	–	–	–	–	2.1	–
$(\mathrm{C_2H_3Co})^+$	–	–	–	–	1.8	16.1
Co^+	14.2	18.4	18.2	22.6	18.5	24.2

[a] $\mathrm{L} = (\mathrm{CH_3})_n\mathrm{Cp}$.

Since NMR and IR studies of these analogs [5,6] in their electronic ground state showed no significant difference in the effects of methyl substitutions in a $\mathrm{CpM(CO)_3}$ fragment, the different fragmentation path was most probably due to different electron relaxation energies during the ionization of the metal atom [23]. In order to elucidate to the effects a transition metal atom from a different period and the degree of methyl substitution of the Cp ring have on fragmentation of M^+ in cyclopentadienyl carbonyl complexes, mass spectra of methyl analogs of $\mathrm{Me}_n\mathrm{CpM(CO)_2}$ (M = Co, Rh; n = 0–5) were also investigated.

The intensities of the molecular (M^+) and the fragment ions of the $\mathrm{Me}_n\mathrm{CpM(CO)_2}$ analogs (n = 0–5) as the total ionic current are listed in Tables 4 and 5. It is seen from these values that, as in the case of the tricarbonyl analogs of Mn [21] and Re [22], the intensity of the molecular ions is unaffected by the presence or number of methyl substituents in the Cp ring. This is probably due to the fact that: (i) the π-interaction of Cp ring and CO group with the metal atom is possible because of the different symmetries of the metal orbitals of [16] and, (ii) the degree of π back-donation $\mathrm{M}d \to \pi^\star(\mathrm{CO})$ must decline rapidly during the ionization of the metal atom [24]. Each of the molecular ions undergoes successive losses of CO

Table 5

Intensities (as total ion current) of Rh-containing ions in mass spectra of $(\mathrm{CH_3})_n\mathrm{CpRh(CO)_2}$ (n = 0–3, 5, 70 eV)

Ions	n				
	5	3	2	1	0
M^+	6.6	8.4	9.3	10.4	11.5
$(M-\mathrm{CO})^+$	9.8	11.8	13.2	14.4	15.3
$(M-2\mathrm{CO})^+$	40.6	38.5	39.7	39.4	57.7
$(M-2\mathrm{CO}-\mathrm{H})^+$	3.5	4.1	3.4	4.0	0.7
$(M-2\mathrm{CO}-2\mathrm{H})^+$	20.8	17.3	19.1	15.8	0.7
$(M-2\mathrm{CO}-4\mathrm{H})^+$	5.2	6.6	8.21	–	–
$(M-2\mathrm{CO}-6\mathrm{H})^+$	2.5	1.2	–	–	–
$(M-2\mathrm{CO}-8\mathrm{H})^+$	1.0	–	–	–	–
Rh^+	6.7	12.4	6.6	15.9	13.1

groups. As in the case with other investigated mononuclear complexes of first-row transition metals, no doubly charged metal-containing ions are present in the mass spectra.

The mass-spectra of $Me_nCpM(CO)_2$ are also different from those of mononuclear polymethylcyclopentadienyltricarbonylmanganese complexes. Whereas Mn–$CpMe_n$ bond breakage is a characteristic fragmentation for $CpMn(CO)_3$ methyl homologs after decarbonylation, a significant loss of H_2 molecules from methyl groups is observed for the Co and Rh analogs. This brings the investigated Co and Rh complexes closer into line with analogous rhenium series for which extensive H_2 loss was observed in the mass spectra (at $n > 1$) [22]. Loss of hydrogen from $Me_nCpM(CO)_2$ was usually observed after both the CO groups had been removed, but in the $CpRe(CO)_3$ analogs it was usual for the $(M\text{-}2CO)^+$ fragment ions still bearing the last CO group to undergo loss of are hydrogen from the Me groups as phenomenon that is characteristic of Co and Rh derivatives (Table 4 and 5). The Rh derivatives probably form fulvene-like ions which were also previously found in mass spectra o polymethylcyclopentadienyl complexes of first-row transition metals (Ti, Cr, Co, Ni) [11,25,26,27].

The other prevalent ions $(ML - H_2)^+$ ($L = Me_nCp$, $n > 1$) are best represented as structures [6] in which a hydrogen molecule is removed simultaneously from different Me groups present in the Cp ring. In contrast to the molecular ions, the intensities of the $(ML - H_2)^+$ ions increase monotonously with growth of n, which correlates well with the higher Me dehydrogenation rates and stabilities of these ions. However, the intensities of ML^+ ions preceding the $(ML - H_2)^+$ ions decline slightly when the first Me group is attached to the Cp ring, and further growth of n has no significant effect. In principle, the change in the number of Me groups should affect the intensities of ML^+ ions since the photoelectronic spectra (He(I), He(II)) of $Me_nCpM(CO)_2$ ($n = 0,5$, M = Co, Rh) [17] indicate that as soon as $n = 5$ the energies of the π-orbitals (e_1) of Cp increase markedly (about 1 eV). This change in intensity of ML^+ is probably determined by a kinetic factor (at $n = 1$) which is further (at $n = 2$–5) compensated by a progressive increase in stability.

Apart from the $(LCo(CO)_2)^+$ ions and their fragmentation products, the mass spectra of the Co species under study showed negligible amounts of ions corresponding to those of the sandwich complexes (cobalticinium analogs) viz., methylcyclopentadienylcyclopentadiene, and methylcyclopentadienylfulvene. The appearance of these ions is probably due to the decomposition of the dimeric cyclopentadienylcarbonylcobalt complexes formed from $Me_nCpCo(CO)_2$ after removal of carbonyl groups and subsequent elimination of the Co atom.

The $Me_nC_5H_{5-n}Co(CO)_2$ complexes ($n = 0$–5) were prepared by procedures published previously [28,29], as were the rhodium complexes $Me_nC_5H_{5-n}Rh(CO)_2$ ($n = 0$–2), [30]; and those with $n = 3$–5 [31].

The ^1H, ^{13}C and ^{17}O NMR spectra are recorded on a Bruker-WP-200-SY spectrometer at 200.13, 50.31 and 27.13 MHz, respectively. The mass spectra were recorded on a MS-30 instrument.

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