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^{17}O, ^{13}C, ^{1}H NMR AND IR SPECTROSCOPIC INVESTIGATIONS OF $(CH_3)_nC_5H_{5-n}Re(CO)_3$ ANALOGUES ($n = 0$–5)

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Summary

^{13}C, ^{1}H NMR investigation of the $(CH_3)_nC_5H_{5-n}Re(CO)_3$ (Me_nCpReT) $n = 0$–5 analogous series showed that the signals of almost all magnetic nuclei shift upfield with increase in n, which also occurs in $(Me_nCp)_2M$ compounds ($M = Fe^{2+}$, Co^{3+}; $n = 0$–5). The smaller value of the $C(CH_3)$ signal (1.5 ppm.) shifts upfield when a further methyl group is introduced into the vicinal position, this shift can be attributed to the absence of the second methyl cyclopentadienyl ring. It is noteworthy that methyl cyclopentadienyl ring coordination to the transition-metal atom results in the downfield shift of the substituted carbon atom (C_{key}) signal. One of the reasons for such a shift might be the reduction in screening effect of the central Cp–M bond π-electron current on C_{key} owing to nodal properties of Cp ring e-orbitals. The δ $^{13}C(CO)$, δ $^{17}O(CO)$, and $\nu(C{\equiv}O)$ values reflect successive increases of Re → CO π-back donation with increase in n.

Introduction

Electronic effects of the substituents in the sandwich and semi-sandwich cyclopentadienyl complexes of transition metals have been published [1–6]. However, the nature of these effects is involved and cannot always be amenable to descriptive interpretation. It is sufficiently difficult to give quantitative theoretical assessment of perturbations in the electron distribution of the complexes when hydrogen atoms are replaced with other substituents. Comparative experimental studies on the spectroscopic properties of variously substituted cyclopentadienyl complexes with

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different transition metals is a reasonable way of tackling this problem. For example, investigation of the methyl analogues of ferrocene and cobalticinium isoelectronic systems with ^{13}C NMR [5,6] has revealed a pattern of conformational interactions by methyl groups and has given an empirical method for predicting the position of $^{13}C(Me)$ nuclei signals in an NMR spectrum for any member of this series.

Results and discussion

This paper examines ^{1}H, ^{13}C and ^{17}O chemical shifts (δ) (Tables 1 and 2) and IR spectroscopic data ($\nu(CO)$) (Table 4) for an analogous series $(CH_3)_nC_5H_{5-n}Re(CO)_3$ ($n = 0$–5). It can be seen from Tables 1 and 2 that the changes in chemical shifts of ^{1}H and ^{13}C nuclei are similar to those previously found for the analogous ferrocene and cobalticinium series $(Me_nCp)_2M$ $M = Fe^{2+}$, Co^{3+} ($n = 0$–5) [5,6]. Increasing the number of methyl substituents, tends to shift the ^{1}H and ^{13}C signals upfield (Tables 1 and 2). This upfield shift of ^{1}H and ^{13}C signals with increasing n seems to be a general feature of the compounds where the poly(methyl cyclopentadienyl) ring is coordinated to the ML fragment ($L = (CO)_2$, $(CO)_3$, $(CO)_2R$, $(CH_3)_nCp$) and is a compromise between electron and steric interactions in cyclopentadienyl ligand and

TABLE 1

^{17}O, ^{13}C NMR CHEMICAL SHIFT DATA FOR COMPLEXES $(CH_3)_nC_5H_{5-n}Re(CO)_3$ ($n = 0$–5; solvent, CH_2Cl_2; relative to ^{13}C TMS and ^{17}O H_2O; in ppm)

Compound [a]	C(CH) [b]	C_{key}	$C(CH_3)$ [b]	C(CO) [b]	$^{17}O(CO)$ [b]
$CpRe(CO)_3$	84.89	–	–	194.26	346.13
$CH_3CpRe(CO)_3$	84.19	107.17	13.72	195.11	
	83.70				
$1,3(CH_3)_2CpRe(CO)_3$	83.83(1)	106.26	13.78	195.98	
	82.49(2)				
$1,2,4(CH_3)_3CpRe(CO)_3$	83.01	104.26(1)	13.66(1)	196.83	
		102.86(2)	12.05(2)		
$(CH_3)_4CpRe(CO)_3$	80.95	101.35	12.24	197.68	345.38
		100.29	10.60		
$(CH_3)_5CpRe(CO)_3$	–	98.85	10.66	198.62	345.22

[a] $Cp = C_5H_{5-n}$. [b] The data for the groups in parentheses, are given as relative intensities.

TABLE 2

^{1}H NMR CHEMICAL SHIFT DATA FOR COMPLEXES $(CH_3)_nC_5H_{5-n}Re(CO)_3$ ($n = 0$–5, solvent $CDCl_3$, relative to TMS; in ppm)

Compound	H(Cp) [a,b]	$H(CH_3)$ [b]
$C_5H_5Re(CO)_3$	5.374	–
$CH_3CpRe(CO)_3$	5.228	2.229
$1,3(CH_3)_2CpRe(CO)_3$	5.072(1) 5.063(2)	2.186
$1,2,4(CH_3)_3CpRe(CO)_3$	5.060	2.152(1) 2.146(2)
$(CH_3)_4CpRe(CO)_3$	4.993	2.153
$(CH_3)_5CpRe(CO)_3$	–	2.153

[a] $Cp = C_5H_{5-n}$. [b] The data for the groups in parentheses are given as relative intensities.

TABLE 3

THE VALUES OF THE DOWNFIELD CHEMICAL SHIFTS $\Delta\delta C_{key}$ IN SOME COMPLEXES (relative to δ C(Cp) in the corresponding unsubstituted ring)

Compound	$\delta C_{key} - \delta C_{C_5H_5}$	Ref.
$CH_3C_5H_4Na^+$	10.7	[a]
$CH_3C_5H_4Re(CO)_3$	22.28	[a]
$CH_3C_5H_4Mn(CO)_3$	19.62	[a]
$(CH_3C_5H_4)_2Co^+$	18.91	6
$(CH_3C_5H_4)_2Fe$	15.92	5

[a] This work.

the effect of other ligands. Furthermore, a number of features caused by the presence of carbonyl groups and different structures also occurs. One is the relatively smaller upfield shift for almost all nuclei of the cyclopentadienyl ligand coordinated to $Re(CO)_3$ as compared to corresponding polymethylferrocenes, which is due to the presence of acceptor carbonyl ligands in CpReT analogues *. Another salient feature of Me_nCpReT systems is that the introduction of a new methyl group into the vicinal position results in an upfield shift of the C(Me) signals from the previous methyl group by 1.5 ppm. This upfield shift, however, is less than in the $(Me_nCp)_2M$ systems, $M = Fe^{2+}$, Co^{3+} ($n = 0$–5) [5,6] where it was 2.0 to 2.1 ppm. This implies that steric interactions between the adjacent methyl groups also play an important part in changing $\delta C(CH_3)$ in CpReT analogues even though the second cyclopentadienyl ligand is not present. The observed difference of 0.5 to 0.6 ppm may be due to steric interactions between the methyl groups of the two cyclopentadienyl ligands present in Cp_2Fe and Cp_2Co^+ analogues but not in the CpReT series. As to steric interactions between methyl groups and carbonyl ligands, the contribution of this effect is of course considerably smaller.

Still another characteristic feature of ^{13}C-NMR spectra for methyl homologues $CpRe(CO)_3$ is the considerable deshielding of C_{key} (about 22 ppm) when a methyl group is replaced by hydrogen. The results in Tables 1 and 3 indicate that introduction of a methyl group into the ring leads to deshielding both in the complexes (16 to 23 ppm), and in the cyclopentadienyl anion (about 10.7 ppm). Moreover, $MeCp^-$ coordination with a transition metal atom brings about additional (6 to 13 ppm) deshielding of C_{key}. This raises two questions: the reason for this downfield shift, and why it occurs at one of the maxima for the methyl analogue of CpReT.

To gain some insight into this effect it is essential to consider the fact that magnetic shielding of the nuclei is in the form of a tensor [8]. It has been reported by Waugh and Pines that in polycrystalline samples, methyl substituents at the ferrocene or aromatic ring have an almost "spherical" tensor of magnetic shielding around the ^{13}C nucleus [9–11] (126, 105 and 96 ppm in durene [10]). This implies that the carbon nucleus remains substantially unchanged at any orientation of the molecule in the liquid in relation to the magnetic field, which results in the ^{13}C

* An exception is the value of δ C(Me) in Me_nCpReT ($n = 1,2$) (Table 1). In $(Me_nCp)_2Fe$ ($n = 1,2$), δ C(Me) is 14.32 ppm and 14.19 ppm, respectively [5], which can most probably be ascribed to a higher degree of freezing the ring current of the electrons by $Re(CO)_3$ with stronger acceptor properties [7].

signals appearing upfield, just where we usually see CH_3 signals. From molecular symmetry, unsubstituted aromatic carbons have an almost axial magnetic shielding tensor, with $\sigma_{\parallel}$ close to average isotropic shielding in a methyl group; however, $\sigma_{\perp}$ is shifted downfield by almost 200 ppm. Since in thermal motion a molecule can occupy not only longitudinal or transverse orientation but also any other orientation in relation to the magnetic field, with an equal degree of probability, each of these orientations has its own shielding value (NMR frequency, ν) while the signal amplitude at ν is given by:

$$g(\nu) = (\nu_{\parallel})^{-1}[1 + 2(\nu - \nu_1)/\nu_{\parallel}]^{-1/2}$$

From this expression, averaging gives the value of chemical shift in the ligand (δ_1) as being at the point dividing the interval between $\delta_{\perp}$ and $\delta_{\parallel}$ in the ratio of 1 : 2.

In the case of C_{key} it has been shown experimentally that ^{13}C nucleus shielding tensor is triaxial, i.e. it is characterized by the asymmetry parameter $\eta = (\delta_{xx} - \delta_{yy})/\Delta\delta$ than by magnetic anisotropy $\Delta\delta = \delta_1 - \delta_{\parallel}$ [11]. It was suggested that the averaging interval of ^{13}C chemical shift exhibits additional expansion in this case: along with a maximum at the $\nu_{\perp}$ frequency corresponding to perpendicular orientation of the molecule in relation to the magnetic field, in addition, a broad area of signals appears in the weaker field. The width of this area is determined by η while the mean chemical shift of this ^{13}C nucleus, with triaxial shielding tensor $\delta_{|||}$, is further shifted downfield with respect to the signal from the unsubstituted aromatic carbon by a value which is proportional to η.

It follows from the above that the great downfield shifts of C_{key} signals near alkyl substituents which are always observed in π-cyclopentadienyl compounds of transition metals can be traced to the fact that replacement of H in the C–H bond with a Me to form a C–C bond has very little effect on $\nu_{\parallel}$ and $\nu_{\perp}$ while a considerable asymmetry parameter appearing in this substitution insures the invariance of the side-effect. For hetero substituents, all these principal values of the C_{key} shielding tensor will be largely influenced by the substituent properties and the average shift can be determined from the shielding tensor asymmetry and from the total electron density at the key atom and other conventional parameters which affect NMR chemical shift. In methyl cyclopentadienyl ligand complexes of transition metals, additional deshielding can be due to a reduction of shielding influence of π-electron current in the central Cp–M bond [12], which is commonly regarded as the primary reason for upfield shift of ligand nuclei signals from π-complex formation [13]. It is true that introduction of a methyl substituent results in increasing low-symmetry distortion in a cyclopentadienyl ligand and removing the degeneracy of e-orbitals (e_{1g} and e_{2g}) [14]. Nodal properties of these orbitals begin to manifest themselves and this possibly results in reduced electron current of the Cp–M bond in C_{key} of the complexes [15] (Fig. 1). On increasing the number of methyl groups on Cp ring in Me_nCpReT (Table 1), an upfield shift of C_{key} signal is observed, as is the case for other analogous series [5,6]. This is in agreement both with electron-donor properties of the methyl group and with the decrease in the influence of the nodal characteristics of the e-orbitals in the cyclopentadienyl ring on C_{key}, as the number of methyl groups is increased.

The other explanation of the downfield shift for the methyl cyclopentadienyl fragment signal seems to be due to considerable elongation of the exocyclic C–R

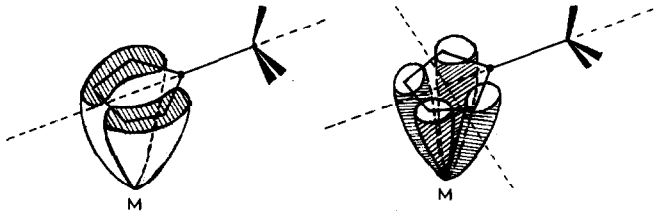

Fig. 1. The nodal properties of the (−) components of Cp *e*-orbitals.

bond when hydrogen is substituted by a methyl group (1.54 Å instead of 1 Å). This results in the electron pair of the C_{key}–$C(CH)_3$ bond, shielding the C_{key} nucleus to a lesser extent compared to the former C–H bond, thus increasing its effective charge. Consequently, the electronic radius $2p$ (r_{2p}) in C_{key} will be reduced and this, according to [16], will increase the (r_{2p}^{-3}) term of the paramagnetic component of ^{13}C chemical shift, i.e., C_{key} will be deshielded [17]. Strong deshielding of substituted carbon C_{key} (Table 3) in MeCpReT is related to the presence of a strongly accepting $Re(CO)_3$ fragment [18–20] which tends to deplete the π-electron density of the Cp ring thus making the substituted carbon more sensitive to low-symmetry perturbation of the methyl group. Similar dependence of C_{key} deshielding on Cp → M donor-acceptor interaction is also observed in related complexes, $(MeCp)_2M$ M = Fe^{2+}, Co^{3+}, where stronger interaction of Cp with Co^{3+} brings about a greater downfield shift of the C_{key} signal when H is substituted by a methyl group (Table 3).

The presence of carbonyl groups in Me_nCpReT molecules enables one to trace the electronic effect of methyl groups on the nuclei of ^{13}C and ^{17}O (CO) groups. It follows from the chemical shifts (δ) of ^{13}C (CO) (Table 1) that the interaction of methyl substituents involves carbonyl ligands. With the increasing number of methyl substituents, the ^{13}C (CO) signals tend to shift downfield. A similar trend was previously found for arenetricarbonyl complexes of chromium and molybdenum, $(CH_3)_nC_6H_{6-n}M(CO)_3$ [21] and is in agreement with electron-donor properties of methyl substituents. As with $(CH_3)_nC_6H_{6-n}M(CO)_3$ M = Cr and Mo [21], the downfield shifts of ^{13}C (CO) in Me_nCpReT can be ascribed to back-donation of metal *d*-electrons to anti-bonding π^*-orbitals of CO ligands, which results in

TABLE 4

THE FREQUENCIES OF THIS STRETCHING VIBRATIONS (ν) OF THE C≡O BOND IN Me_nCpReT (n = 0–5) IN $CHCl_3$.

Compound [a]	ν(C≡O) (cm^{-1})	
	A	E
$CpRe(CO)_3$	2033	1941
$CH_3CpRe(CO)_3$	2029	1937
$1,3(CH_3)_2CpRe(CO)_3$	2027	1936
$1,2,4(CH_3)_3CpRe(CO)_3$	2023	1931
$(CH_3)_4CpRe(CO)_3$	2021	1929
$(CH_3)_5CpRe(CO)_3$	2018	1927

[a] $Cp = C_5H_{5-n}$.

decreased shielding of the carbon nucleus in CO groups. This is confirmed by the stretching vibration frequency (ν) of the C≡O bond in Me_nCpReT (Table 4): increasing n results in lower values of ν, which implies antibonding of the C≡O bond. This is also indicated by chemical shifts of the ^{17}O nuclei in carbonyl ligands (Table 1) which, as n increases, are shifted slightly upfield probably owing to the bonding π-electrons in the C≡O bond being drawn towards the oxygen atom as a result of the dative M → CO interaction [21].

The Me_nCpReT complexes studied were synthesized by a conventional technique [22]. The ^1H, ^{13}C and ^{17}O NMR spectra were obtained on a Bruker-WP-200 SY NMR spectrometer at 200.13, 50.31 and 27.13 MHz, respectively.

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