Hydrogen bonds and conformations of α-carbinol derivatives of cyclopentadienyltricarbonyls of manganese and rhenium

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Abstract

On the basis of IR spectra and molecular mechanics calculations, the conformations stabilized by hydrogen bonding in α-carbinol derivatives of cyclopentadienyltricarbonyl manganese and rhenium have been determined. Intramolecular H-bonds with Mn and Re atoms are found in the tertiary carbinols. Relative stability of the OH · · · M hydrogen bonds increases in accordance with metal basicity (Mn < Re) and on going from the carbonyl to the triphenylphosphine ligand. The proton-donating ability of these carbinols is quantitatively characterized. Competition exists between intra- and intermolecular H-bonds of different types upon self-association in the crystal.

Introduction

The conditions for the formation of intramolecular hydrogen bonds (IHB) of OH · · · M type (M = Fe, Ru, Os), the sequence of chelate cycle stability and the influence of steric effects in α-metallocenylcarbinols have been discussed in previous papers [1–5]. The aim of this work is to examine the interrelation between conformation and hydrogen bond formation of α-carbinol derivatives of cyclopentadienyltricarbonyl manganese (CTM) and rhenium (CTR). Three types of carbinol with a wide variety of substitutes were chosen.

IR spectra were combined with conformational calculations using the molecular mechanics method [6]. Spectra were measured in CCl_4 in the $\nu(OH)$ and $\nu(CO)$ regions under conditions which excluded self-association in the solid and molten state. The proton-donation ability was determined by spectra measured in a $CCl_4/DMCO$ mixture as the standard proton-accepting solvent.

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(I)   (II)   (III)
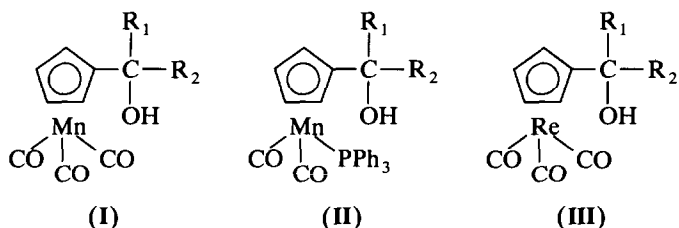
R_1 = H, R_2 = H(a), Me(b), Ph(c), CTM(d), CTR(f), Fc(e)

R_1 = Me, R_2 = Me(g), CTM(h)

R_1 = Ph, R_2 = ^{t}Bu(i), Ph(j), CH_2Ph(k), 4-$OCH_3C_6H_4$(l), CTM(m), CTR(n)

Results and discussion

1. The character of hydrogen bonds and conformations

In order to better understand the role of steric effects of carbinol group substitutes, let us consider the results of a conformational calculation for the molecules of primary, secondary (R = Me, Ph) and tertiary ($R_1 = R_2 = $ Ph) carbinols of cymantrene (I). The conformational energy (U_{conf}) was calculated as a function of torsion angle $CCCO(\phi)$ characterizing the position of the OH group in the Cp ring.

(1)   (2)
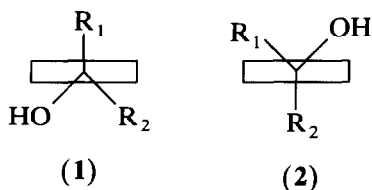
A similarity has been established between conformational features of these and metallocenylcarbinols [1–3]. The plot of U_{conf} for primary carbinols does not reveal the regions corresponding to the sufficiently stable conformations (Fig. 1(1)). For the secondary carbinols, the minima become more pronounced; they are displayed in the regions of the positive and negative values of the ϕ angle, corresponding to conformations 2 and 1 (Fig. 1(2)).
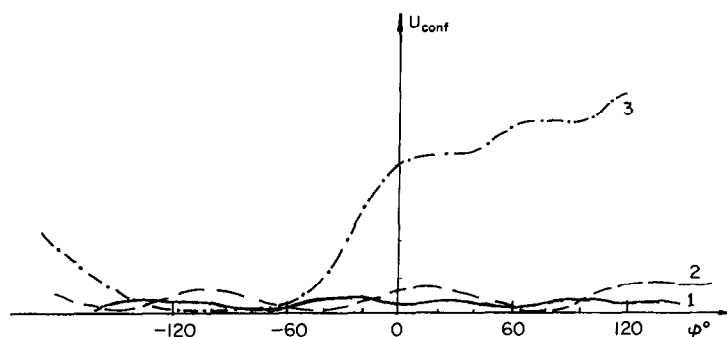

Fig. 1. Plot of U_{conf} (kcal/mol) versus ϕ (the angle of rotation of the carbinol group around the C–C bond) in carbinols: $(CO)_3MnC_5H_4CR_1R_2OH$ ($R_1 = R_2 = $ H (1); $R_1 = $ H, $R_2 = $ Me (2); $R_1 = R_2 = $ Ph (3))

Table 1

IR spectral data for $(CO)_3Mn(C_5H_4)CRH$ OH (I), $PPh_3(CO)_2Mn(C_5H_4)CRHOH$ (II) in CCl_4

R	I			II		Assign-	I	II	Assign-
	$\nu(OH)$ (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	$A \times 10^{-4\,a}$	$\nu(OH)$ (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	ment	$\nu(CO)$ (cm^{-1})	$\nu(CO)$ (cm^{-1})	ment
H(a)	3626	28	0.17	3622	29	$\nu(OH)$ free	2026	1937	A
							1943	1873	E
Me(b)	3621	35	0.36	3612	38	$\nu(OH)$ free	2024	1936	A
	low ass.			3585s			1943	1872	E
Ph(c)	3615	21	0.56	3616	31	$\nu(OH)$ free	2024	1936	A
	low ass.			3580s			1943	1872	E
CTM(d) [b]	3608	28	0.40	3606	46	$\nu(OH)$ free	2024	2023	A
	low							1936	E, A
	ass.						1948	1879	E
Fc(e)	3610s					$\nu(OH)$ free	2024	–	A
	3571	44	–			$\nu(OH \cdots Fe)$	1948	–	E

[a] A, l/mol cm^2. [b] IIIf: R = CTR, $\nu(OH) = 3608$ cm^{-1}, low ass., $\Delta\nu_{1/2} = 41$ cm^{-1}.

The conformational curves for the tertiary carbinols ($R_1 = R_2 = Ph$) point to an increased steric influence. Conformation 2 with the OH group situated above the Cp ring becomes unfavorable; only one very broad minimum is in the region corresponding to conformation 1, $\phi < 0$ (Fig. 1). The conformation features for these carbinols and more complicated manganese complexes [6] are identical. The conformation with the OH group rotated towards the metal atom as in many secondary α-metallocenylcarbinols is energetically favorable [7].

Thus, the results of the conformation calculations show that the steric factors do not impose a limitation on the hydrogen bonding with the metal atom; moreover, for tertiary carbinols they have to assist in the H-bonding formation.

As can be inferred from Tables 1, 2, the spectral picture in the region of OH depends on these steric effects. The spectra of the primary carbinols in dilute CCl_4 solutions show only $\nu(OH)(free)$ bands (Table 1). The position (3622–3625 cm^{-1}) and half-band width ($\Delta\nu_{1/2} = 26–28$ cm^{-1}) correspond to the stretching vibration of free OH groups in common organic carbinols [8].

The spectra of the secondary carbinols (Table 1) exhibit the bands in the lower frequency region (3606–3616 cm^{-1}) but such a position $\nu(OH)(free)$ is characteristic for secondary carbinols in comparison with primary ones [8]. The anomalous broadening of these bands ($\Delta\nu_{1/2} = 38–45$ cm^{-1}), the increase of integral intensity (Table 1) compared with alcohols [8] and the low frequency asymmetry allow us to suggest the contribution of the $\nu(OH)$ (bond). An increase in the value of $\Delta\nu_{1/2}$ and low frequency asymmetry for the carbinols of rhenium in comparison with those of manganese gives evidence for stabilization of the conformer with an intramolecular H-bond of OH $\cdots$ M type.

The spectra of the tertiary carbinols exhibit several bands (Table 2). A high frequency band (3598–3611 cm^{-1}) with $\Delta\nu_{1/2} = 15–22$ cm^{-1} was assigned to the $\nu(OH)(free)$. The low-frequency shift of this band and a decrease of the $\Delta\nu_{1/2}$ value in comparison with primary and similar secondary carbinols is the same as

Table 2

IR spectral data for $(CO)_3Mn(C_5H_4)CR_1R_2OH$ (I), $PPh_3(CO)_2Mn(C_5H_4)CR_1R_2OH$ (II), $(CO)_3Re(C_5H_4)CR_1R_2OH$ (III) in CCl_4

N	R_1/R_2	ν(OH) (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	$\Delta\nu$ (cm^{-1})	N	ν(OH) (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	$\Delta\nu$ (cm^{-1})	Assignment
Ig	Me/Me	3611	26	–	IIg	3602	16		ν(OH) free
		ass.				3570	30	32	ν(OH $\cdots$ M)
Ij	Ph/Ph	3611	17		IIj	3610	24		ν(OH) free
		3565	40	46		3520	50	90	ν(OH $\cdots$ M)
Ii	Ph/^{t}Bu	3616			IIi	3610	16		ν(OH) free
		3598	60			3590			
		3571		35		3552	40	58	ν(OH $\cdots$ M)
Ik	Ph/CH$_2$Ph	3610s			IIk	3602	20		ν(OH) free
		3570	22	40		3571	40	31	ν(OH $\cdots$ π(Ph))
Il	Ph/ArOCH$_3$	3610	15		III	3611	26		ν(OH) free
		3550	40	60		3530	50	81	ν(OH $\cdots$ M)
Ig	Me/CTM	3610	23	–	IIIg	3606	30	–	ν(OH) free
		low				low			
		ass.				ass.			ν(OH $\cdots$ M)
Im	Ph/CTM	3609	28		IIIn ^{a}	3602	80	42	ν(OH) free
		3570	40	39		3560			ν(OH $\cdots$ M)
IIIi	Ph/Ph	3609	15						ν(OH) free
		3545	40	64					ν(OH $\cdots$ M)

^{a} R_1 = Ph, R_2 = CTR.

the change in these parameters in the usual alcohols [8]. The second rather weak band in the region 3520–3570 cm^{-1} with $\Delta\nu_{1/2}$ = 40–60 cm^{-1} was interpreted as ν(OH) (OH $\cdots$ M). This assignment is in accordance with the data of conformational analysis and is confirmed by the low frequency shift of this band on going from Mn to Re in $(CO)_3MC_5H_4C(Ph)_2OH$ (Ij, IIIj). In the case of hydrogen bonding with a Cp ring, we should see a high frequency shift of ν(OH) (bonded OH) because the π-electron density in CTR is less than in CTM [9].

The spectra of carbinols with a bulky ^{t}Bu-substitute turned out to be very interesting. There are three bands ν(OH) in the spectra of $(CO)_3MnC_5H_4C(OH)$ (^{t}Bu)Ph (Ii) 3610, 3590, 3552 cm^{-1} and in $PPh_3(CO)_2MnC_5H_4C(OH)(^tBu)Ph$ (IIi) 3616, 3598, 3571 cm^{-1}. In order to assign the observed bands, we investigated the temperature dependence. Upon cooling of solutions, the relative intensity of the high frequency band (Fig. 2a, b) decreased. The bands, 3552 (Ii) and 3571 cm^{-1} (IIi), broadened, shifted to the low frequency region and their intensity increased. The same temperature changes were observed in the spectrum of $(CO)_3ReC_5H_4CPh_2OH$ (IIIj).

It is impossible to account for these differences by the influence of low temperature on the position of ν(OH) [10]. It is obvious that they reflect the higher occupation of the conformations favorable for the OH $\cdots$ M bond. The ν(OH) (free) bands, as is known, are narrower in the carbinols with bulky substitutes [8]. Therefore, we succeeded in observing two bands belonging to the free OH group vibrations in some different conformers (3610–3616 cm^{-1} and 3590–3598 cm^{-1}). These conformations are likely to depend on the rotation around the C–O bond because the rotation around C–C bonds has no influence on the position of
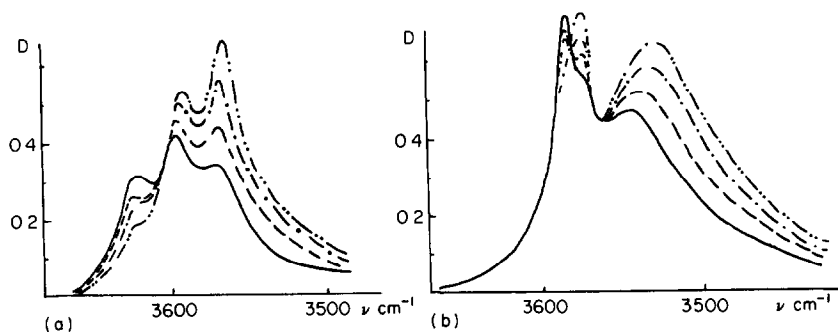
Fig. 2. IR spectra of solutions in CCl_4 ($c = 2.5 \times 10^{-3}$ mol/l, $d = 2$ cm). IR spectra of $(CO)_3MnC_5H_4CPh(C(CH_3)_3)OH$ (a) $(CO)_2PPh_3MnC_5H_4CPh(C(CH_3)_3)OH$ (b) solutions in $CCl_4/CHCl_3$ (1:1), for different temperature: $T = 293$ K (— ·· —), 253 (— · —), 223 K (— — —), 198 (————).

ν(OH)(free) [8]. The low frequency component of this doublet, increasing with cooling, belongs to the more stable conformer without IHB. The conformer **1** with an H bond of OH · · · M type (bands 3552 and 3571 cm^{-1}, Fig. 2) is the most stable.

Thus, intramolecular hydrogen bonds are formed with Mn and Re atoms only if there are some energetically favorable conformations with the position of the OH group under the Cp ring as in ferrocenylcarbinols [1].

2. Proton-donating properties

The proton-donating ability of OH groups is determined in order to define its influence on the chelate cycle stability. The spectral ($\Delta\nu$) and thermodynamic ($-\Delta H$) parameters of the carbinol interactions with DMSO as a standard electronodonor were obtained (Table 3).

The substitution of the CO group by PPh_3 causes essential weakening of the proton-donating properties while going from CTM (I) to CTR (III) derivatives; these changes are rather small. For instance, if $R_1 = R_2 = Ph$, the values of ΔH for Ij and IIj are 5.1 and 4.7 kcal/mol, respectively, but for IIIj, 5.3 kcal/mol.

Table 3

Spectral characteristics and enthalpies ($-\Delta H$ kcal/mol) for the intermolecular hydrogen bonds of α-carbinols with DMSO [a]

Carbinol	ν(cm^{-1})	$\Delta\nu$(cm^{-1})	$-\Delta H$ (kcal/mol)	Carbinol	ν(cm^{-1})	$\Delta\nu$(cm^{-1})	$-\Delta H$ (kcal/mol)
Ia	3363	262	4.8	IIa	3377	245	4.6
Ib	3365	255	4.7	IIb	3374	238	4.5
Id	3304	309	5.4	IIIf	3280	328	5.6
Ig	3365	246	4.6	IIg	3392	208	4.0
Ij	3324	287	5.1	IIj	3357	253	4.7
Ii	3388	228	4.3	IIi	3446	166	3.4
Ik	3355	255	4.7	IIk	3397	215	4.1
Il	3330	280	5.0	III	3364	246	4.6
Ih	3305	305	5.4	IIIi	3310	299	5.3
Im	3283	326	5.6	IIIn	3250	352	5.9

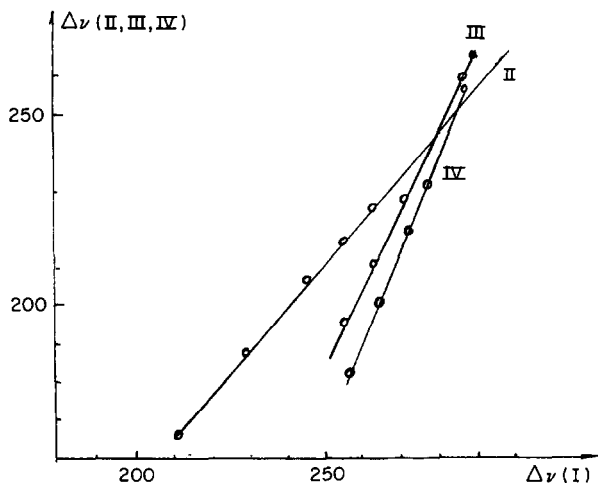[a] $c_{DMSO} = 5.6 \times 10^{-3}$ mol/l, $c_{carbinol} = 5 \times 10^{-3}$ mol/l

Fig. 3. Linear relation between the $\Delta\nu(OH \cdots OS(CH_3)_2)$ of carbinols $(CO)_3MnC_5H_4CR_1R_2OH$ (I), $(CO)_2PPh_3MnC_5H_4CR_1R_2OH$ (II) $FcCR_1R_2OH$ (III), $Fc^9CR_1R_2OH$ (IV).

Good linear correlations have been established between the characteristics of the proton-donating ability of different types of carbinol (Fig. 3). These parameters depend on the electronic effect of substitute R for every class of carbinol (Table 3, Fig. 3).

Analysis of the different class data indicates that proton-donation properties of α-carbinol CTM derivatives are greater than those of α-ferrocenylcarbinols [3] (Fig. 3). However, sensitivity to the substitute influence is greater for the latter type of carbinols (see the difference between the angles of lines I and III).

3. Relative stability of the intramolecular H bonds

The data obtained (Tables 2, 3) led us to conclude that the relative stability of the intramolecular H bonds is mainly dependent on the electron-donating properties of the metal. The influence of the proton-donating ability is considerably weaker.

Thus, the relative stability of the OH $\cdots$ M H-bond type ($\Delta\nu$) grows if one CO ligand is substituted by an electron-donating PPh_3-group (Fig. 4), while as we have shown, the proton-donating ability decreases. As a measure of the relative stability, we used the $\Delta\nu(OH) = \nu(\text{free OH}) - \nu(\text{bonded OH})$ values [1].

On changing the manganese atom by rhenium, the stability of the H bond increases (Fig. 4). For all similar carbinols (Mn < Re) the values of $\Delta\nu(OH)$ increase. The same regularities have been reported for α-metallocenylcarbinols (Fe < Ru < Os) [3]. Unfortunately, we cannot compare the relative stability ($\Delta\nu$) of chelate cycles of Mn and Fe carbinols, because these compounds are not isostructural. But the values of formation constants provide very interesting information. The ability to form the intramolecular hydrogen bond of OH $\cdots$ M type is, to a great extent, weaker for CTM and CTR carbinols than for ferrocenylcarbinols. The values of K_f for the latter compounds are considerably larger.

Thus, on changing the metal atom down the group the stability of the intramolecular hydrogen bond of OH $\cdots$ M type increases in parallel with the basicity of M [3].
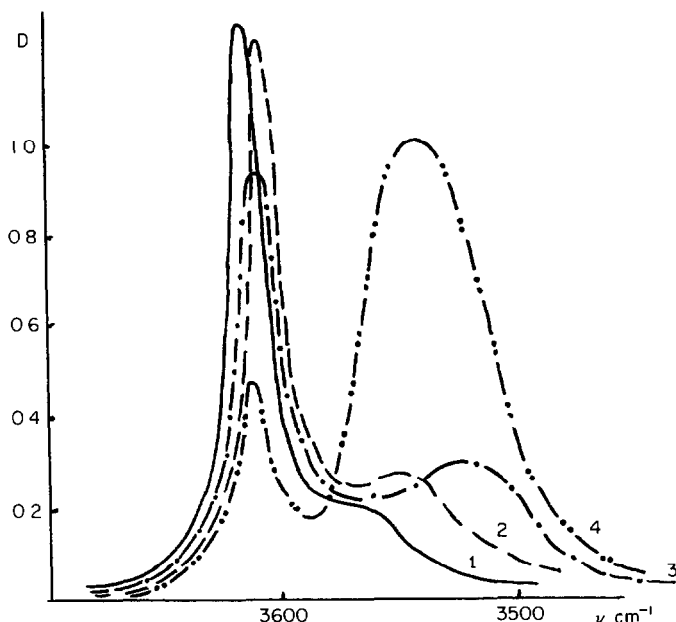
Fig. 4. IR spectra of carbinols: $(CO)_3MnC_5H_4CPh_2OH$ (1); $(CO)_3ReC_5H_4CPh_2OH$ (2); $(CO)_2PPh_3MnC_5H_4CPh_2OH$ (3); $FcCPh_2OH$ (4); solutions in CCl_4 ($c = 5 \times 10^{-3}$ mol/l, $d = 2$ cm).

4. Competition between different hydrogen bonds in solution and in the solid state

We examined the possibility of a competition between different types of hydrogen bonds in solution and in the solid state.

It was interesting to examine spectra of the carbinol which has both cymantrenyl and ferrocenyl substitutes, i.e. $(CO)_3MnC_5H_4CH(Fc)OH$ (Ie). The spectra of this compound in solutions and in the solid state are identical and as it turned out they are similar to those of $Fc(CH)(OH)C_5H_4Cr(CO)_3$ [5]. They have only one band ν(bonded OH) 3563 cm^{-1}. There is no doubt about the assignment for this band to ν(OH $\cdots$ Fe). The formation of such a chelate cycle is in accordance with the greater ability of the Fe atom to form a hydrogen bond (K_f OH $\cdots$ Fe $\gg K_f$ OH $\cdots$ Mn).

It is not clear whether this reflects electron-accepting properties of CO ligands, or the metal atom position in the Periodic Table. To answer this question, an investigation of some structurally analogous carbinols is necessary.

π-Electron density can compete with the metal atom if the geometry of the cycle formed is favorable. Such a situation is possible for carbinols with benzyl substitutes (Ik, IIk). There is a possibility of forming a five-membered cycle with a hydrogen bond of OH $\cdots$ π type. Actually, the manganese atom is not an electron-donating center in the compounds $(CO)_3MnC_5H_4C(Ph)(OH)CH_2Ph$ (Ik) and $(CO)_2PPh_3MnC_5H_4C(Ph)(OH)CH_2Ph$ (IIk). In this case, the PPh$_3$ ligand does not increase the stability of the hydrogen bond in the carbinol (IIk) (Table 1). The band ν(bonded OH) is assigned to the hydrogen bond with the π-electron density of the benzyl ring. It is noteworthy that this weak intramolecular H bond is

preserved in the solid state, the spectra of these compounds being similar in the crystal state and in solution.

Previously we have shown [4] that a competition between the intramolecular H bond of OH $\cdots$ M type and intermolecular bonds in the solid state is possible. The preservation of the chelate cycle is either due to the influence of greater steric hindrances precluding the association or due to high stability of cycles ($\Delta\nu > 100$ cm^{-1}, $i.e.$ OH $\cdots$ Os) [4].

Intramolecular hydrogen bonds with Mn and Re atoms are weak ($\Delta\nu < 100$ cm^{-1}); therefore, one can hardly expect their presence in secondary carbinols without bulky substitutes (Ib, c).

In fact, there are no IHB bands in the spectra of secondary carbinols except those of Ie carbinols. These spectra are similar to those of the primary carbinol (Ia) with no cycles.

The spectra reveal broad ν(OH $\cdots$ O) bands in the region 3450–3350 cm^{-1} ($\Delta\nu_{1/2} > 100$ cm^{-1}). An assignment of these bands is based on the linear relation-

Table 4

IR spectra of α-carbinols in the solid state (in Nujol)

N	R_1/R_2	ν(OH) (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	Assignment	ν(CO) (cm^{-1})
Ia	H/H	3350	410	ν(OH $\cdots$ O)	2016, 1932
Ib	H/Me	3384	320	ν(OH $\cdots$ O)	2024, 1944
Ic	H/Ph	3450	130	ν(OH $\cdots$ O)	2024, 1943
Id	H/CTM	3598	18	ν(OH)(free)	2032, 2017, 1943
		3463	60	ν(OH $\cdot$ $\cdot$ O)	
Ig	Me/Me	3588	10	ν(OH $\cdot$ OC)	2020, 2012, 1940, 1912
		3476	60	ν(OH $\cdots$ O)	
Ih	Me/CTM	3582	7	ν(OH $\cdots$ OC)	2026, 2012, 1956, 1932, 1900
		3464	30	ν(OH $\cdots$ O)	
IIg	Me/Me	3584	10	ν(OH $\cdot$ OC)	1930, 1922 1867, 1857
		3468	60	ν(OH $\cdots$ O)	
Im	Ph/CTM	3580	30	ν(OH $\cdots$ OC)	2032, 2022, 1943, 1900
IIIf	H/CTR	3564	76	ν(OH $\cdot\cdot$ OC)	2024, 2020, 1933, 1920, 1900
IIIn	Ph/CTR	3564	6	ν(OH $\cdots$ OC)	2032, 2022, 2016, 2020
IIIh	Me/CTR	3564	18	ν(OH $\cdot\cdot$ OC)	1946, 1935, 1925, 1910, 1888
Ij	Ph/Ph	3565	10	ν(OH $\cdots$ Mn) [a]	2024, 2015, 1940, 1917
		3513	36	ν(OH $\cdots$ O)	
IIIj	Ph/Ph	3541	10	ν(OH $\cdot\cdot$ Re) [a]	2029, 1937, 1912
		3504	37	ν(OH $\cdots$ O)	
Ie	H/Fc	3560	30	ν(OH $\cdots$ Fe) [a]	2020, 1920
		3225	120	ν(OH $\cdots$ O)	1913, 1891

[a] ν(OH $\cdots$ M) intramolecular hydrogen bond.
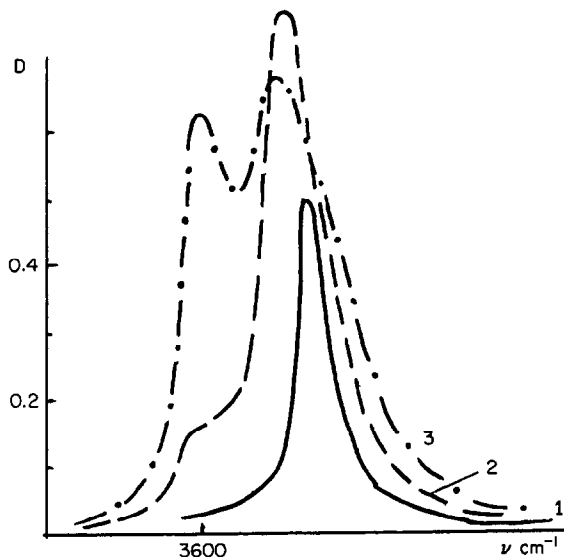
Fig. 5. IR spectra of $(CO)_3MnC_5H_4CPh(CH_2Ph)OH$ (Nujol) (1), solution in CCl_4 (2) and $(CO)_2PPh_3MnC_5H_4CPh(CH_2Ph)OH$ solution in CCl_4 (3) ($c = 5 \times 10^{-3}$ mol/l, $d = 2$ cm).

ship existing between $\Delta\nu$ and $\Delta\nu_{1/2}$ (Table 4), which have been found previously for intermolecular H bonds of OH $\cdots$ O type in McCHROH [4].

A more complicated picture was observed in the spectra of tertiary carbinols and the secondary carbinol with a bulky substitute such as CTM, CTR. An analysis of the spectra allows these compounds to be divided into three groups. IR spectra of the first group of carbinols display two types of ν(bonded OH) bands and four or more ν(CO) bands (Ig, Ih, IIg). There is no question about the assignment of the low frequency bands to the ν(OH $\cdots$ O) vibrations. These bands have slightly higher frequencies and are narrower (ν(OH) 3476–3464 cm^{-1}, $\Delta\nu_{1/2}$ 30–60 cm^{-1}) than those of secondary carbinols due to increased steric hindrances. The high frequency bands (3588–3584 cm^{-1}) we interpret as ν(OH $\cdots$ OC) vibration. First, our assignment is based on the X-ray data for Ih [7]. The crystal of this carbinol is composed of independent molecules connected with two types of intermolecular H bonds: OH $\cdots$ O(OH) and OH $\cdots$ O(CO). In addition, when the temperature of the crystal samples rises to the melting point, the spectra of all this group of carbinols (Ig, IIg, Ih) change in a similar way. The low frequency ν(CO) bands and shoulders (1930–1843 cm^{-1}) disappear, the spectra show the same patterns as for secondary carbinols (Ibc); namely, the band at 3585 cm^{-1} disappears, also thus supporting an assignment of this band to ν(OH $\cdots$ OC). The spectra of molten compounds are similar to those in diluted CCl_4 solutions (Fig. 6). Thus two types of association coexist in the first group: via OH $\cdots$ OC and OH $\cdots$ O hydrogen bonds.

Self-association of only one type, namely, OH $\cdots$ OC, is revealed in the spectra of the second group (carbinols IIIh, IIIf, Im, IIIn). Only one ν(OH) band (3564–3580 cm^{-1}) whose $\Delta\nu_{1/2}$ values vary in the 6–76 cm^{-1} interval (Table 4) is preserved. The spectra in the region of ν(CO) vibrations show the same complicated pattern, as in the case of group I. As one goes from crystal to solution, the
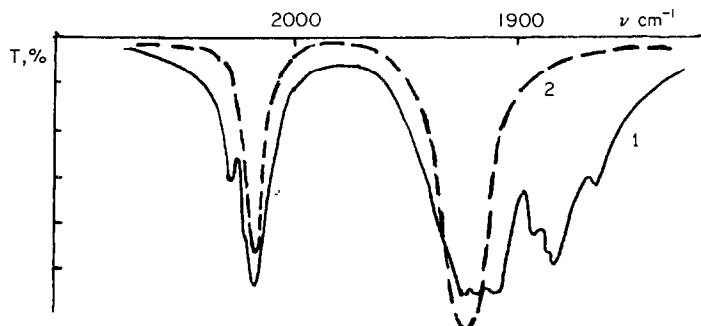
Fig. 6. IR spectra of $[(CO)_3ReC_5H_4]_2CPhOH$ (Nujol) (1), solution in CCl_4 (2) ($d = 0.0127$ cm, $c = 5 \times 10^{-3}$ mol/l).

low frequency bands of $\nu(CO)$ disappear and the spectra resemble those for the diluted solution. An additional proof for the OH $\cdots$ OC type association is a lower frequency position of $\nu(OH)$ for CTR (IIIn) than for CTM (In) derivatives (Table 4), which corresponds to increased electron density on the oxygen atom of the CTR carbonyl group [11].

Finally, two carbinols, Ij and IIIj, belong to the third group. Intramolecular hydrogen bond of OH $\cdots$ M type and the common OH $\cdots$ O type intermolecular bond characterize the solid state of these carbinols (Table 4). The bands $\nu(OH \cdots O)$ are revealed in the more high frequency region than for the above mentioned carbinols (3513–3504 cm^{-1}) which suggests a decrease in self-association ability. The narrow bands (3565 and 3541 cm^{-1}) are similar to the $\nu(OH \cdots M)$ bands observed in the diluted solution spectra. It is impossible to assign these bands to $\nu(OH \cdots OC)$, because the low frequency bands and shoulders lower than 1912 cm^{-1} are absent. The spectra in the region $\nu(CO)$ and $\nu(OH)$ undergo no change in the molten state.

Thus, the different types of intermolecular H-bonds are realized in the solid state (OH $\cdots$ O and/or OH $\cdots$ OC). If the role of steric factors predominates, the chelate cycles can also be preserved.

Conclusion

IR spectroscopy in conjunction with conformational calculations provides information on the relation between conformational mobility of the carbinol group and the formation of chelate cycles in a series of α-carbinol derivatives of Mn and Re cyclopentadienyltricarbonyls. The intramolecular hydrogen bonds with manganese and rhenium atoms have been established first. Such H bonds are weak ($\Delta\nu(OH)$ < 100 cm^{-1}), and formed only if the conformation with the OH group rotated towards the metal atom is energetically favorable (especially in tertiary carbinols). The relative stability of such cycles is more dependent on the electron-donating ability of the metal than on the proton-donating ability of OH group. The stability of OH $\cdots$ M bonds increases on changing the metal atom down the group (Mn < Re) (as for α-metallocenylcarbinols (Fe < Ru < Os)) and on substituting the CO ligand by PPh$_3$. The competition between different types of intra- and

intermolecular hydrogen bonds (OH $\cdots$ M, OH $\cdots$ π, OH $\cdots$ O, OH $\cdots$ OC) in solution and in the solid state appears to be mainly dependent on the steric effects caused by the substitute.

Experimental

The compounds studied were prepared by published procedures [12].

IR spectra were recorded with an M-80 "Specord" spectrophotometer in 5×10^{-3}–5×10^{-2} mol/l CCl_4, CH_2Cl_2, $CHCl_3$ solutions, $d = 0.006$–2 cm. The integral intensities were calculated as described previously [13]. The temperature dependence (295–198 K) was obtained in a $CCl_4/CHCl_3$ mixture (1:1) in an argon atmosphere.

The proton-donating properties were determined in a $CCl_4/DMSO$ mixture, $c_{DMSO} = 0.3$–5.6 mol/l. The enthalpies of the hydrogen bonds, $-\Delta H$, were evaluated using [14] $-\Delta H = 18 \Delta\nu/(\Delta\nu + 720)$. The $\nu(OH)$ values correspond to their centers of gravity. The spectra in the solid state were measured in Nujol in the range 400–4000 cm^{-1}.

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